

**U.S. DEPARTMENT OF COMMERCE
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PB-285 275

Nitrate Removal from Water Supplies by Ion Exchange

Michigan Univ, Ann Arbor

Prepared for

Municipal Environmental Research Lab, Cincinnati, Ohio

Jun 78

United States
Environmental Protection
Agency

Municipal Environmental Research
Laboratory
Cincinnati OH 45268

EPA-600/2-78-052
June 1978

Research and Development

PB 285 275



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TECHNICAL REPORT DATA

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1. REPORT NO. EPA-600/2-78-052		2.		3. PROJECT/INSTR. ACCESSION NO. PB285275	
4. TITLE AND SUBTITLE NITRATE REMOVAL FROM WATER SUPPLIES BY ION EXCHANGE				5. REPORT DATE June 1978 (Issuing Date)	
				6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Dennis A. Clifford* Walter J. Weber				8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS The University of Michigan Ann Arbor, Michigan 48109				10. PROGRAM ELEMENT NO. 1CC614	
				11. CONTRACT/GRANT NO. Grant No. R-803898	
12. SPONSORING AGENCY NAME AND ADDRESS Municipal Environmental Research Laboratory--Cin., OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268				13. TYPE OF REPORT AND PERIOD COVERED Final 8/75 - 12/76	
				14. SPONSORING AGENCY CODE EPA/600/14	
15. SUPPLEMENTARY NOTES Project Officer: Thomas J. Sorg 513/684-7228 *Presently with University of Houston, Houston, Texas 77004 See also Executive Summary, EPA-600/8-77-015					
16. ABSTRACT Anion exchange using synthetic organic resins is a proven and practical technology for the removal of nitrate from water supplies. However, disposal of the spent regenerant brine solution containing nitrate is a potential problem. Two processes were examined in detail in this report--single-bed strong-base anion exchange with NaCl regeneration and two-bed strong-acid, weak-base ion exchange with HCl and NH ₄ OH regeneration. Both systems must be operated to nitrate breakthrough to minimize regeneration costs. The two-bed process is one and one-half to two times as expensive to build and operate as is the single-bed process, but produces softened low-TDS, low-nitrate water, and has a readily disposable, spent regenerant with fertilizer value. Important design considerations were found to include the nitrate and sulfate concentrations in the raw water, the service flow rate, the resin bed depth, and the nitrate/chloride selectivity of the resin. The sulfate, nitrate, chloride, and bicarbonate selectivities and multicomponent column behavior of the anion resins available from U.S. manufacturers were examined and are reported in detail. An important peripheral finding was that significant quantities of non-volatile organics were leached from "clean" resins into the treated water. <					
17. KEY WORDS AND DOCUMENT ANALYSIS					
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group	
Water treatment--ion exchanging, Water supply, Ion exchanging, Ion exchange resins, Demineralizing, Nitrate deposits--inorganic nitrates, Sulfates, Chlorides, Cost estimates, Experimental data		Nitrate removal, Ion exchange--two-bed process		13B	
18. DISTRIBUTION STATEMENT Release to Public		19. SECURITY CLASS (This Report) Unclassified		21. NO. OF PAGES 311	
		20. SECURITY CLASS (This page) Unclassified		22. PRICE A14-A01	

EPA-600/2-78-052
June 1978

NITRATE REMOVAL FROM WATER SUPPLIES BY ION EXCHANGE

by

Dennis A. Clifford
Walter J. Weber, Jr.
The University of Michigan
Ann Arbor, Michigan 48109

Grant No. R-803898

Project Officer

Thomas J. Sorg
Water Supply Research Division
Municipal Environmental Research Laboratory
Cincinnati, Ohio 45268

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

Serious and occasionally fatal poisonings in infants have occurred following the ingestion of water containing concentrations of nitrate. This report presents the results of an investigation on the removal of nitrate from water supplies by two-bed (strong-acid, weak-base) ion-exchange treatment systems, and by single-bed (chloride form) ion-exchange systems. Detailed information is given on nitrate selectivity, rates and capacities for nitrate and competing ions, and regeneration requirements for various commercially available weak-base ion-exchange resins. Also, an economic comparison is made between the single-bed and the two-bed ion-exchange systems.

Francis T. Mayo
Director
Municipal Environmental Research
Laboratory

ABSTRACT

Single-bed strong-base anion exchange with NaCl regeneration is currently the method of choice for removal of nitrate from water supplies. In non-arid non-coastal locations, disposal of regenerant brine from such a system is a definite problem. An alternative ion-exchange process comprising a strong-acid cation exchanger followed by a weak-base anion exchanger with bypass blending of raw water and regeneration with HNO_3 and NH_4OH has been proposed. In addition to nitrate reduction, the process would yield low hardness water and produce a regenerant easily disposed of as a fertilizer. The process would be operated to nitrate breakthrough with chromatographic elution of less-preferred ions. A two-phase study was undertaken; Phase I to determine the anion resin characteristics associated with high nitrate selectivity in the presence of sulfate, chloride, and bicarbonate, and Phase II to establish the column elution behavior of these anions as a function of the process variables: resin type, fluid detention time, and raw water composition.

Thirty-two commercially available anion resins, thirteen weak-base and nineteen strong-base, with various polymer matrices, amine functionalities, capacities, degrees of cross-linking, and pK_a 's were evaluated for sulfate/nitrate, chloride/nitrate and bicarbonate/nitrate selectivity in .005 N acid solution. Binary isotherms, and H_2SO_4 , HNO_3 , and HCl titration curves were developed. Average separation factors were determined and related to resin properties.

The sulfate/nitrate separation factor (α_N^S) had an extreme range of variability (1.7 - 137) with matrix and functionality being primary determinants. A hypothesis relating distance of charge separation to selectivity is proposed; when the exchange sites are incorporated into the resin polymer backbone at a guaranteed-close distance, the resin is very divalent ion selective. The effect of functionality was verified; the sulfate selectivity sequence is polyamines > tertiary > quaternary, but it is argued that the effect is due more to size than to the previously reported basicity.

The nitrate/chloride selectivity (α_{Cl}^N) exhibited a much narrower range of variability (1.85 - 4.33) with matrix and degree of cross linking (porosity) primarily determining its magnitude. High nitrate/chloride selectivity is associated with hydrophobic resins: polystyrene > non-polystyrene and macroporous > gel for non-polystyrene resins.

Carbonic acid was not significantly taken up under the experimental conditions, so the predicted, and verified, resin selectivity sequence is sulfate > nitrate > chloride >> bicarbonate.

Statistical techniques were used to develop predictive equations for α_N^S and α_{Cl}^N as functions of matrix, functionality, and porosity; five such equations are given.

In Phase II, eleven column runs were made with five resins, two different nitrate concentrations (14 and 21 ppm) and two bed depths (31 and 61 cm). Four-component effluent profiles are given for all the runs and nitrate throughput comparisons are plotted to illustrate the effects of the variables.

The important factors influencing the process efficiency

are α_{Cl}^N , equivalent fraction of nitrate in the water (x_N), and detention time. Surprisingly, highly sulfate-selective resins actually increase the relative fraction ($\bar{y}_N$) of nitrate on the resin at breakthrough. Some explanations are proposed for this and a tentative method for calculation of $\bar{y}_N$ based on multicomponent chromatography theory is presented.

Even with operation to nitrate breakthrough the overall chemical efficiency, as meq nitrate removed per meq regenerant, was low (13%) for the representative artificial groundwaters tested.

A regeneration cost comparison between the single and two-bed processes revealed that, with $HCl-NH_4OH$ regeneration, the two-bed costs were triple those of the single-bed $NaCl$ system. However, the two-bed regenerant was estimated to be land disposable whereas the single bed regenerant was not.

One-percent solutions of the resins equilibrated overnight were found to contain 3 to 100 ppm organic carbon. If not eliminated, these extractable organics may cause serious problems in water supply applications.

This report was submitted in fulfillment of Research Grant No. R-803898 by The University of Michigan under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period July 21, 1975, to December 31, 1976.

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LIST OF SYMBOLS AND ABBREVIATIONS

SYMBOLS

*	Denotes multiplication when used between variables
α	Debye-Hückel ion-size parameter
$\text{\AA}$	Angstroms
$\overline{ac}_i$	Activity of ion i in the resin phase, eq/l
ac_i	Activity of ion i in the liquid phase, eq/l
α_{ij}^i	Separation factor for ions i and j , dimensionless
α_{NS}^S	Sulfate/nitrate separation factor, dimensionless
α_{NCl}^N	Nitrate/chloride separation factor, dimensionless
α_{BN}^N	Nitrate/bicarbonate separation factor, dimensionless
C_0	Total, initial liquid phase concentration meq/l
C	Liquid phase concentration, meq/l
$C_{i,0}$	Initial liquid phase concentration of i , meq/l
C_i	Liquid phase concentration of i , meq/l
γ_I	Activity coefficient of i in resin, dimensionless
γ_i	Activity coefficient of i in liquid phase, dimensionless
ϵ	Resin bed void fraction, dimensionless
F	The F statistic in analysis of variance, dimensionless
E_M	Maximum possible chemical efficiency for nitrate removal, dimensionless
E_O	Overall nitrate removal efficiency, dimensionless
E_R	Regeneration efficiency, dimensionless

SYMBOLS

K_a	Protolysis constant for amines
pKa	Negative logarithm of protolysis constant
K_j^i	Selectivity coefficient
K_j^{f1}	Solution phase, corrected selectivity coefficient
Q	Resin exchange capacity, meq/ml, meq/gm
R_I	Relative crystal ionic radius dimensionless
ρ	Density of resin gms/ml
q	Resin phase concentration, meq/ml, meq/gm
r	Correlation coefficient, dimensionless
r^2	Coefficient of determination, dimensionless
TEC	Total Equivalent Capacity of resin, meq/ml
τ	Superficial detention time, minutes
T	Throughput, eq. solution/eq. exchanger
x_i	Equivalent fraction of ion i in liquid phase, dimensionless
x_B	Equivalent fraction of bicarbonate in liquid phase, dimensionless
x_{Cl}	Equivalent fraction of chloride in liquid phase, dimensionless
x_N	Equivalent fraction of nitrate in liquid phase, dimensionless
x_S	Equivalent fraction of sulfate in liquid phase, dimensionless
y_i	Equivalent fraction of ion i in solid phase
$\bar{y}_i$	Average equivalent fraction of ion i on the resin at the end of the run, dimensionless
$\bar{y}_N$	Average equivalent fraction of nitrate on the resin at the end of the run, dimensionless

SYMBOLS

Ve	Bed volumes of feed to nitrate breakthrough, dimensionless
V	Total bed volumes of feed solution
v	Volume of resin bed, ml, l
Z	Valence of ion, dimensionless

ABBREVIATIONS

ANOVA	Analysis of Variance
DETA	Diethylenetriamine
HCHO	Formaldehyde
ISO	Isoporous
$\text{LOG}_e \text{ S/N}$	$\text{Ln } \alpha_N^S$ (used in statistical tables)
$\text{LOG}_e \text{ N/Cl}$	$\text{Ln } \alpha_{\text{Cl}}^N$ (used in statistical tables)
$\text{NO}_3\text{-N}$	Nitrate concentration measured as nitrogen, mg/l
N2POSITN	Dummy Variable indicating whether nitrogen is in the matrix (N2POSITN = 1.0) or out of the matrix (N2POSITN = 0.0)
NAS	National Academy of Science
PA	Polyamine functionality
POLY	Polyamine functionality
Q-1	Quaternary amine, type 1
Q-2	Quaternary amine, type 2
Quat.	Quaternary amine
RSIZE	Dummy variable indicating relative size of amine functional group; polyamines = 2.0, tertiary = 2.19, quaternary = 2.36
"R"	Amine functional group

ABBREVIATIONS

$\overline{R}$	Overbar denotes resin phase
$\underline{R}$	Organic radical, $-\text{CH}_3$, $-\text{C}_2\text{H}_4\text{OH}$ etc.
R_a	Ratio of area below isotherm to area above isotherm
SIGNIF	Statistical level of significance
$\overline{S}^i$	Denotes abrupt transition zone in resin concentration profile where species i is absent downstream
SBA	Strong-base anion
STY-DVB	Styrene-divinylbenzene
TDS	Total dissolved solids
TETA	Tetraethylenetriamine
X	Liquid phase equivalent fraction
WBA	Weak-base anion
XLINKING	Dummy variable indicating relative degree of crosslinking: isoporous = 0.5, microporous = 1.0 and macroporous = 2.0

ACKNOWLEDGMENTS

The following persons are acknowledged for their assistance in the accomplishment of this work:

Tom Sorg EPA project officer for his interest and cooperation during the length of the study.

R. Anderson and Dr. I. Abrams of the Diamond Shamrock Chemical Company and D. Harrington of the Dow Chemical Company for their very informative discussions on the composition and properties of ion-exchange resins, and Dr. Judd Posner for his helpful theoretical discussions.

Professor W.A. Ericson Director of the U-M Statistical Research Lab for his assistance with the statistical analysis and the interpretation of statistical results.

Steve Reiber, Ann Farrell, Jeff Meyers, Linda Burns and Bill Hodgins for their work in the laboratory and in the preparation of the computer data plots.

Jill Schultz for her work in typing this and earlier drafts, and Tom Hadfield and Diane Rumps for their help in typing the initial drafts of this difficult manuscript.

SECTION 1

INTRODUCTION

It is anticipated that the provisions of the U.S. Safe Drinking Water Act of 1974 (Public Law 93-523) will apply to all public water systems in mid 1977. Incorporated into that act is a provision which, when it takes effect, will legally limit the concentration of nitrate as nitrogen to 10 mg/l. This level is equivalent to the long-standing, recommended limit established by the U.S. Public Health Service for the prevention of methemoglobinemia in infants. Public and private water supplies in nearly all of the fifty states and in many foreign countries have been found to be polluted with nitrates in amounts regularly exceeding this 10 mg/l limit. Nitrate removal by ion exchange with synthetic, organic, anion-exchange resins is the treatment method which appears to offer the most readily available, proven technology at a cost which is not unreasonable. However, disposal of the spent nitrate-containing, regenerant-brine solution is an unsolved problem and, previous to the time of this research, there was a lack of technical information in the literature regarding the selectivity of the various anion exchange resins for nitrate with respect to the important ground-water anions: chloride, sulfate and bicarbonate. Neither was there sufficient, useful information available for the prediction of multicomponent effluent concentration profiles from ion-exchange columns economically operated by chromatographically eluting the ions not intended to be removed.

The research described here was undertaken to provide the missing data and to propose hypotheses concerning the prediction and control of anion exchange selectivity in general. A further objective was to provide a means of describing the multicomponent chromatographic column behavior of anion-exchange resins, especially weak-base resins, in nitrate removal service. A final objective was to perform technical and economic evaluations comparing a conventional, single-bed, strong-base, nitrate removal process to a two-bed, strong-acid, weak-base, nitrate removal process which would produce a spent ammonium nitrate regenerant amenable to disposal as a fertilizer.

SECTION 2

CONCLUSIONS

PHASE I: RESIN SELECTIVITY STUDY

Nineteen strong-base and thirteen weak-base resins were tested for sulfate, nitrate, chloride and bicarbonate selectivities. These selectivities were then related to the following resin properties: matrix, functionality, porosity, capacity, pKa and type.

Sulfate was always preferred over nitrate by all the strong and weak-base resins tested. These synthetic polymers exhibited an extremely wide range of selectivities. For strong-base resins $\alpha_N^S = 1.71$ to 3.37 , and for weak base resins $\alpha_N^S = 2.67$ to 137 . It is expected that the sulfate preference will hold true for any of the resins tested here with ground waters having total dissolved solids concentrations up to at least 3000 ppm, i.e., 0.06 N as CaCO_3 .

Nitrate was always preferred over chloride by all the anion resins tested although the range of preferences was relatively narrow. For strong base resins: $\alpha_{\text{Cl}}^N = 2.85 - 3.64$ and for weak-base resins: $\alpha_{\text{Cl}}^N = 1.70 - 4.86$. As expected this separation factor was independent of total solution concentration.

Bicarbonate and carbonic acid were not significantly taken up by the ion-exchange resins in binary equilibrium with dilute

HNO₃. The expected selectivity sequence has been verified as sulfate > nitrate > chloride >> bicarbonate.

The average separation factor, α_j^i , as measured by the ratio-of-areas technique proposed here, provided an adequate sulfate/nitrate isotherm description and an excellent chloride/nitrate isotherm description.

Resins with relatively low sulfate selectivity ($\alpha_N^S = 2-4$) had modestly "S" shaped isotherms explained by their tendency to have sterically constrained sites of unequal preference for divalent sulfate. Resins with high sulfate selectivity ($\alpha_N^S = 13-137$) had smooth-shaped isotherms, and titration curves with inflection points for divalent H₂SO₄ but not for monovalent HCl or HNO₃; it is hypothesized that these latter resins have a preponderance of pairs of appropriately spaced sites available for divalent-ion interactions.

Matrix was the single most important factor in the determination of both α_N^S and α_{Cl}^N and consequently of nitrate selectivity in general. If the electrostatically active nitrogen atoms are in the continuous polymer structure, as they are with all but the polystyrene resins where the active nitrogen is pendant on the polymer structure, then the resin is highly sulfate selective. This, it is hypothesized, is due to the almost-guaranteed proximity of two active nitrogen atoms which are expected to be separated by about 4.48 Å in the polymer backbone. This distance derives from the nitrogen separation distance of one ethylene group in the amine monomers: diethylenetriamine--DETA, and triethylenetetraamine--TETA, commonly used to provide functionality and crosslinking in anion exchange resins. For both entropic and electrostatic reasons, these properly spaced, protonated amines much prefer multivalent ions to univalent ions.

High nitrate/chloride selectivity tended to be associated with polystyrene resins and highly crosslinked (macroporous) non-polystyrene resins. These categories of resins are more hydrophobic than are the microporous non-polystyrene resins which demonstrated lower nitrate/chloride selectivities.

Functionality was nearly as important as nitrogen-nitrogen site proximity in determining sulfate selectivity but had no apparent effect on the nitrate/chloride preferences of resins. The size of the nitrogen functional group seems to be the determining factor; larger functional groups tend to prevent the required proximity of a pair of nitrogen atoms. Furthermore, these large groups hinder the approach of the mobile counterions to the positively charged nitrogen centers.

Porosity was a major determinant of sulfate selectivity, among Type I strong-base anion resins where isoporous resins with a relatively low degree of crosslinking were considerably more sulfate selective ($\alpha_N^S = 2.98$) than were the more-cross-linked gel and macroporous resins ($\alpha_N^S = 1.82$).

Type II, strong-base anion resins had higher sulfate selectivity ($\alpha_N^S = 2.99$) than did the Type I resins ($\alpha_N^S = 1.82$). Since the major difference here is basicity, it appears that reducing the basicity increases sulfate selectivity.

Predictive equations developed by an optimization of the multiple regression analysis procedure, have verified that, when considering all possible variables and all resins, the most important determinants of sulfate/nitrate selectivity are matrix and functionality while matrix and relative degree of crosslinking are the primary determinants of the magnitude of nitrate/chloride selectivity. Nevertheless, within particular subclasses of resins, other factors such as type and basicity (pKa) do have

significant further influences on α_N^S and α_{Cl}^N .

PHASE II: MULTICOMPONENT CHROMATROGRAPHIC COLUMN STUDIES

E_M , the maximum possible chemical efficiency in nitrate removal service, has been defined as being equal to the average equivalent fraction of nitrate on the exhausted resin ($\bar{y}_N$). This $\bar{y}_N$ will be greater than x_N if the resin concentrates nitrate by eluting the lesser preferred species (H_2CO_3 and Cl^-) in chromatographic fashion until nitrate breakthrough. The most important influence on $\bar{y}_N$ is, predictably, x_N ; when it's low, process efficiency will be correspondingly low because the exhausted resin will contain mostly sulfate and chloride -- species not intended to be removed. A tentative procedure based on multi-component equilibrium theory has been developed which correctly predicts $\bar{y}_N$ given the composition of the feedwater and the relevant selectivities -- α_{Cl}^N and α_N^S .

Short detention times ($\tau < 3.0$ min), shallow beds (depth < 60 cm) and high exhaustion rates (> 2.5 gal/min ft³) reduced $\bar{y}_N$ by causing relatively more chloride, apparently the kinetically favored anion, to be on the resin at nitrate breakthrough.

Nitrate/chloride selectivity (α_{Cl}^N) was the most important selectivity in determining the relative amount of nitrate on the resin at nitrate breakthrough.

Sulfate/nitrate selectivity (α_N^S) was nearly irrelevant in determining the average equivalent fraction of nitrate on the resin at the end of a run. Surprisingly, slight increases in the relative amount of nitrate on the resin are possible as a result of increasing rather than decreasing the sulfate selectivity -- α_N^S . The simplified explanation offered for this is that: (1) all the sulfate will be removed from the feedwater regardless

of its actual selectivity because it is the most preferred species and, (2) high sulfate selectivity promotes a short sulfate-rich zone near the column entrance in which almost no nitrate is removed thereby leaving essentially all of that species to compete with the lesser preferred chloride in the second equilibrium zone of the column which is where nearly all of the nitrate is concentrated.

Nitric acid was found to be unacceptable as a regenerant in the two-bed process even though it would have greatly enhanced the fertilizer value of the regenerant wastewater. It is too costly, 46.5¢/1000 gal treated water ($12.3¢/m^3$), requires excess cation bed rinsing to reduce nitrate and allows the possibility of disastrous nitrate and acid pollution of the water supply in the event of an operating error. Even though HCl is more costly than H_2SO_4 , it may be more economical where low concentration and large excesses of H_2SO_4 are required due to potential $CaSO_4$ fouling of the cation resin.

It has been determined here that a regeneration level of 300% of the theoretical HCl required must be applied to the cation bed if calcium and magnesium are the primary cations on the resin. Levels much lower than that cause premature cation breakthrough, increasing pH and reduced anion bed capacity with smaller values of $\bar{y}_N$ at breakthrough. High regeneration levels on the other hand maximize $\bar{y}_N$ but may cause unacceptably low effluent pH forcing termination of the run. A level of 300% or greater will also be required for NaCl regeneration of the single-bed process.

High column capacities can improve the overall economic efficiency of the ion-exchange process if they lead to lower rinse volume requirements but, since high capacity resins also tend to be highly sulfate selective and require progressively longer rinse volume with service time, that possible improvement

in operating efficiency is not guaranteed.

Net bicarbonate removal was zero, as expected for both the two-bed and single-bed processes. Thus, high values of bicarbonate in the raw water don't measurably influence $\bar{y}_N$. Bicarbonate and carbonic acid apparently have a catalytic effect in columnar ion-exchange processes so it is tentatively concluded that a system degasifier should be located downstream from the anion bed rather than preceding it.

A summary of the advantages (+) and disadvantages (-) of the single-bed and two-bed processes follows:

Single-bed, strong base anion with NaCl regeneration

- (+) Simple, no balancing of beds and regenerants
- (+) Low cost regeneration
- (-) Very difficult and costly to dispose of regenerants in non-coastal locations where natural evaporation is impossible
- (-) Iron must be removed to prevent resin fouling
- (-) Continuous nitrate analysis required for process control

Two-bed, strong-acid, weak-base, NH_3 & HCl regenerants

- (+) Partial softening in addition to nitrate removal
- (+) No problem with iron fouling. Precipitated iron is removed from the cation bed during each regeneration
- (+) Regenerants wastewaters expected to be easy to dispose of by land application as fertilizer
- (-) Complex system: bed sizes and regenerants must be balanced
- (-) Degasifier for CO_2 control required
- (-) Continuous pH and nitrate analysis required for process control
- (-) High regenerant costs

Wherever it can be used, the single-bed process will be cheaper than the two-bed process. A comparative process economic evaluation reveals that the two-bed process with NH_3 and HCl as regenerants has chemical plus disposal costs which are approximately 50% higher than the single-bed process. Those costs are 27.84/1000 gal ($7.34\text{¢}/\text{m}^3$) and 18.4¢/1000 gal ($4.86\text{¢}/\text{m}^3$) respectively assuming the two bed regenerants are given away as fertilizer, while the single bed regenerants are trucked 8 miles for dilution disposal into a stream. If regenerant disposal isn't a consideration the chemical costs for the two-bed system are triple those of the single-bed system.

Organic extractables present in the anion resins even after "conditioning" give rise to total organic carbon (TOC) concentrations in the 3-100 ppm range in acidic, aqueous solutions containing about 0.9% resin for 16-20 hours. It is anticipated that the extractable organics in both cation and anion resins represent a potential problem in water supply where they might be chlorinated to produce carcinogens.

The acceptable anion resins for nitrate removal service are as follows considering that high nitrate/chloride selectivity, high capacity and moderate sulfate/nitrate selectivity are the desirable characteristics:

Acceptable

STY-DVB, Polyamine, Gel Resins
STY-DVB, Tertiary Amine, MR Resins
STY-DVB, Quat. (I&II) Amines, Gel, MR & ISO
Acrylic-Amine, Polyamine, MR Resins
Phenol-HCHO, Polyamine, MR Resins

Unacceptable

Epoxy-Amine, Polyamine Gel Resins
Acrylic-Amine, Tertiary Amine, Gel Resins
Aliphatic-Amine, Polyamine Gel Resins

The overall chemical efficiency (E_0) can be expected to be about 13.3% for both the single-bed and two-bed processes. This is based on the observed average equivalent fraction of nitrate on the resin at the end of the runs ($\bar{y}_N = .40$) with a feedwater containing the same equivalent concentration of nitrate, chloride and sulfate and an irrelevant amount of bicarbonate which undergoes no net removal in either process. This overall chemical efficiency has been defined as the equivalents of nitrate removed per equivalent of regenerant supplied and is the product of $\bar{y}_N$ and E_R , the regeneration efficiency, which has been determined to be 0.33 based on a regeneration level of 300%.

SECTION 3

RECOMMENDATIONS

The degree to which various cation and anion resins yield leachable organic compounds from breakdown of their polymer structures should be quantified and the compounds identified. These unwanted hydrocarbons are likely to be chlorinated during the traditional, water supply disinfection practices with the subsequent formation of possible carcinogenic compounds. The problem has some degree of urgency as the legal provisions of the 1974 Safe Drinking Water Act will necessitate the more widespread use of synthetic organic ion exchangers as the best available water treatment technology for removal of trace ionic contaminants, viz.: toxic metals, fluoride and nitrate.

The mathematical models available for the description of multicomponent ion exchange should be modified to accommodate the apparent acid-adsorption behavior of the kinetically-slow, weak-base resins. These modified models should be amenable to computer solution using numerical methods of analysis. There is sufficient experimental data in this report to initially verify a mathematical model of the multicomponent behavior of ground waters containing nitrate, chloride, sulfate and bicarbonate fed to and eluted from weak or strong-base, anion-exchange columns.

Polymer research should be undertaken with the objective of designing ion exchange polymers which will be selective for monovalent-nitrate ions over divalent-sulfate ions based on the

findings that the distance of nitrogen functional group separation is the most significant factor in univalent/polyvalent ion separations. This proposed research work differs markedly from the many previous attempts at designing nitrate-selective resins by incorporating nitrate-specific organic radicals into the resins; resins designed on that basis had severe polymer stability problems and were nearly impossible to regenerate because of their nitrate specificity. Such is not expected to be the case with the proposed polymers although low ion-exchange capacity might be a problem.

Combination water treatment systems incorporating reverse osmosis for TDS reduction and ion exchange for nitrate removal should be investigated.

Pilot plant studies of the single-bed and two-bed ion-exchange systems described here should be undertaken to verify the cost estimates, assess the relative design and operational complexities, and evaluate the alternative means of regenerant disposal especially land application as a fertilizer. These studies might best be done in a geographic location where fluoride is also a problem. Fluoride is expected to be the least-preferred ion, and control of the process by monitoring the effluent for fluoride by ion-selective electrode would seem to be practical.

The anticipated, beneficial, catalytic effect of carbonic acid and bicarbonate ions on the nitrate removal efficiency of anion exchangers in multicomponent ion-exchange service should be investigated. Results of such an investigation should resolve the question of whether to place the system degasifier upstream or downstream of the anion exchanger.

SECTION 4

THEORETICAL CONSIDERATION

THE NITRATE PROBLEM -- BACKGROUND

Sources of Nitrate

Nitrate nitrogen ($\text{NO}_3\text{-N}$) is occasionally found in ground water supplies at concentrations significantly above the long-standing, recommended limit [125] and the interim legal limit of 10 mg/l [127]. Common sources of this nitrate pollution are: (1) nitrified percolation from septic-tank tile fields, (2) drainage and infiltration of fertilizer and feed-lot nitrogen and, (3) ground water recharge operations using high-rate infiltration of secondary sewage effluents. The first two sources generally give rise to $\text{NO}_3\text{-N}$ in the range of 20-50 mg/l [84, 109, 130] while the third produces ground waters in the 10-30 mg/l range due to oxidation of the NH_4^+ in the recharge water by the aerobic soil bacteria [16, 17, 28, 58]. Increasingly higher food production and semi-rural population density throughout the U.S., coupled with the pressing need to recharge ground water supplies in semi-arid and coastal locations will serve to worsen the $\text{NO}_3\text{-N}$ problem in the near future.

Nitrate appears to be accumulating in many of our ground waters at an alarming rate. Geographically, the ground water nitrate problem is very widespread in rural, suburban and even urban areas. Recently documented problems have been reported

in Fresno, California [109, 130] and Long Island, New York [130], Kentucky [96, 129], Missouri [110], North Carolina [24], Texas [50, 117], Wisconsin [33], Georgia, Iowa, Minnesota, Kansas, Oklahoma and Illinois [123], and in Europe [29] and specifically in England [49]. A recent bibliography with abstracts by Lehman [79] and a bibliography by Summers [116] list numerous references to this ubiquitous problem.

The seriousness of the health problem continues to be debated because of the difficulty and expense of removing nitrate from water and because the nitrate pollution is largely rural and diffuse. Nevertheless, the National Academy of Science Committee on Nitrate Accumulation [91] concluded in 1972 that, even though infant methemoglobinemia had been nearly eradicated in the United States: "The Public Health Service recommended limits for nitrate in drinking water [10 ppm $\text{NO}_3\text{-N}$] should not be relaxed," and further that: "Equipment for removing nitrogen from drinking water should be devised for use in homes and on farms. Among the possible methods are microbiological denitrification and anion-exchange resins" [Reference 91 p. 74]. The NAS report reiterates that, since records have been kept, 350 cases of methemoglobinemia have been reported in the U.S., mostly in the years 1945-1950. An estimated 2000 cases have been reported in North America and Europe since 1945 with a 9% infant mortality rate [91].

Finally, it should be noted that the nitrate ion is much more toxic to mammals than is the relatively nontoxic nitrate ion, [93, 91] and it is nitrite, not nitrate that is responsible for infant deaths due to methemoglobinemia. The water quality standards limit the more stable and ubiquitous nitrate ion concentration because nitrate may be reduced to nitrite in the gastrointestinal tract, especially in infants. In the stomachs of ruminant mammals, e.g., cattle, nitrate is readily reduced to nitrite and death due to methemoglobinemia can occur

within 2-5 min. after ingestion [23,91].

Nitrate Removal Processes

Conventional water treatment processes including coagulation, filtration and chlorination have little effect on the NO_3^- concentration of raw water. The high solubility of all the common nitrate salts and the lack of co-precipitation and adsorption of the nitrate anion are primarily responsible for its perseverance in these processes.

Advanced water treatment processes appear to be limited to ion exchange with synthetic, anion resins. Nitrate rejection by cellulose-acetate reverse-osmosis membranes is low (50-85%) compared to HCO_3^- (80-98%), $\text{SO}_4^{=}$ (99-100%), and Cl^- (86-97%) [133]. Distillation and electrodialysis can usually be eliminated from consideration because of their high cost for treating low (less than 3000 ppm) TDS waters [133], a consideration also applying to reverse osmosis where it has been estimated to be 10 times as costly as ion exchange at 10 ppm $\text{NO}_3\text{-N}$ in a 450 ppm TDS water (See discussion in Ref. 40). Biological denitrification, [114,115] the preferred method for treating wastewaters, has been demonstrated to be technically feasible but its high cost, long detention times (1-2 hours), increased use of chlorine to eliminate bacteria and nitrite, and the requirement for post aeration and filtration would seem to preclude its use for treatment of public and private water supplies.

Previous studies using anion exchange for nitrate removal from secondary sewage effluent and agricultural drainage have met with considerable success. Eliassen found, on a pilot scale that, nitrified secondary effluent containing 18 ppm $\text{NO}_3\text{-N}$, 65 ppm $\text{SO}_4^{=}$ and 200 ppm Cl^- could be successfully treated for nitrate removal using diatomaceous earth filtration and anion exchange for about 21¢/1000 gallons (1965 dollars, not including

brine disposal) [44, 45, 46]. In these tests the anion selectivity was $\text{SO}_4^{=}$ > NO_3^- > NO_2^- > Cl^- > HCO_3^- for the type II, a strong-base anion resin Duolite A-102-D. The findings of Midkiff and Weber [87] which were derived from type I, strong-base, anion column experiments are in accord with this selectivity sequence. Additional data regarding selectivity with strong-base resins can be found in a review by Sabadell [107] and in Table I of reference 56 where $\alpha_{\text{Cl}}^{\text{N}}$ is in the range of 2--3.

The Search for Nitrate Selective Resin

The search for a highly nitrate-selective resin has dominated several investigations. Grinstead and Jones [55] described the development of a very nitrate-selective ($\text{NO}_3^-/\text{Cl}^- = 20/1$ and $\text{NO}_3^-/\text{SO}_4^{=}$ >> 20/1) adsorbent for wastewater treatment. Their system comprised a macroreticular, polystyrene resin without functional groups into which was adsorbed a nitrate-selective amidine reagent dissolved in an organic solvent. This they have termed the "extractant-in-bead-approach". Its one advantage was high nitrate selectivity with respect to sulfate, chloride, and bicarbonate. Its disadvantages were low capacity (in meq/ml) compared to conventional ion-exchange resins, and the continuous loss of organic solvent and extractant into the treated water.

"Entirely inadequate capacity" was a disadvantage of the nitrate selective resins prepared by Meloan and Gran [85] who chemically incorporated nitrate-selective, organic reagents into commercially available, weak-base, anion exchangers. While not specifically investigated in that work, the problem of extractable organics leaching into the water supply is also expected to be a significant problem with this approach.

Wallit and Jones [129] succeeded in developing a true, anion-exchanger resin with salinogen functional groups attached

to a polystyrene matrix. Working only with nitrates and chlorides, they obtained nitrate selectivities in the range of 8/1 to 14/1. In fact, the resins were so selective for nitrates that they couldn't be regenerated by ordinary methods, thereby rendering the process commercially unfeasible. Here again extractable organics are expected to cause problems.

The dilemma of high selectivity producing efficient ion exchange with inefficient regeneration due to the very significant stoichiometric excess of regenerant required has been pointed out previously [10, 129]. The desirable selectivity sequence for nitrate removal is regenerant anion $\gg \text{NO}_3^- > \text{SO}_4^{=}$, Cl^- , HCO_3^- with a very low regenerant anion concentration in the raw water. This situation is approached with weak-base, anion resins where hydroxide is the much preferred anion and is essentially absent from the acidic effluent of a strong-acid, cation unit. Finding or producing a nitrate-selective, weak-base resin would help resolve the dilemma, although that is not expected to be an easy task. The nitrate selectivities of commercially available resins were determined in this study.

The generally accepted anion selectivity sequence for both weak and strong base resins is $\text{SO}_4^{=} > \text{NO}_3^- > \text{Cl}^- > \text{HCO}_3^-$ [36, 60, 78, 86, 133]. Verification of the sequence at anion concentrations normally found in groundwaters and wastewaters has been demonstrated by many investigations [10, 44, 49, 56, 86, 87] for strong-base resins. Nevertheless, significant differences in the actual selectivity values among various, strong-base anion resins do exist as demonstrated by Gregory and Dhond who experimented with ten different, strong-base resins and the anions: $\text{SO}_4^{=}$, $\text{HPO}_4^{=}$ and Cl^- [54].

Beulow et. al. [5] clarified the statement by Chemical Separations Corporation that Dowex 21K, strong-base resin was nitrate selective by showing that it was true only at concentra-

tion levels near and above 50 meq/l (2400 ppm $\text{SO}_4^{=}$ or 3100 ppm NO_3^-), concentrations which are of little interest in water supplies. This reversal of selectivity is due to the activity coefficient-concentration relationship and has been previously reported for the $\text{SO}_4^{=}/\text{Cl}^-$ selectivity which inverts in favor of chloride at concentrations above 63 meq/l (2240 ppm Cl^-) [78, 134]. Divalent ions are nearly always preferred over monovalent ions by synthetic organic ion exchangers in the total concentration levels usually found in water supplies [13, 18, 36, 40, 60, 82]. This preference has been termed "electroselectivity" [60].

Iron Fouling of Nitrate Removal Resin

The ferrous iron commonly occurring in ground waters may be converted to ferric iron by dissolved oxygen either in the water prior to contact with the ion-exchange resins or, in the case of cation exchange resins, within the actual resin pores where the resulting, insoluble, ferric iron oxides precipitate and foul the beads [3]. Iron fouling of anion resins is primarily confined to the surface of the beads where it tends to prevent the exchangeable counterions from gaining access to the interior of the beads. Using X-ray scanning techniques on the cross section of a weak-base anion resin used in the desulfatization of sea water, Aveni et. al. [8] verified that the iron fouling was serious but limited to the anion resin bead surface. With simple backwashing and NaCl regeneration, these iron deposits are only partially removed and eventually reduce the exchange capacity to intolerably low levels as experienced by Beulow [10] in a nitrate removal study using strong-base anion resins. Where the fouling is severe, the resins must be removed from the columns (if the columns aren't acid resistant) and washed with acid to dissolve the precipitated iron oxides. Such cleaning is not expected to be required in the case of cation resin beds re-

generated with HCl , H_2SO_4 or HNO_3 which should remove the adhering iron oxides on every regeneration cycle. This can be considered an advantage offsetting the capital and operating cost disadvantages of two-bed (cation-anion) nitrate removal processes when strong acids are used to regenerate the cation resin. Any large-scale, nitrate removal process for ground water supplies must successfully deal with the iron fouling problem or it cannot be considered widely applicable.

The Problem of Regenerant Brine Disposal

The regenerant NaCl and its disposal have been shown or estimated to be the most significant costs when removing nitrates with a single, strong-base, ion-exchange column [10, 66]. Unfortunately, both costs can only increase for alternative systems since NaCl is the lowest cost regenerant available on a \$/lb-equivalent basis. Furthermore, trucking the $\text{NaCl-NaNO}_3\text{-Na}_2\text{SO}_4$ brine to a nearby stream for "dilution" disposal, the low-cost method suggested by Holzmacher [66], cannot be recommended here because of its detrimental, nutrient effect on the receiving stream.

The alternatives for regenerant brine disposal are assumed to be limited to the following:

- (1) ocean outfalls in coastal locations
- (2) evaporation ponds in semi-arid regions
- (3) sanitary sewers where permitted, but only recommended where sewage denitrification facilities exist and where the brine doesn't seriously dilute the sewage
- (4) deep-well injection where permitted, very costly for large volumes of brine
- (5) sale as fertilizer, the most desirable.

For reuse as a fertilizer, the nitrogen content of the brine should be maximized and electrolytes like sodium ions should be

minimized because of their detrimental effects on soils [84, 92, 118]. This effectively eliminates NaCl (and KCl) from consideration.

Bingham [11] has described a two-bed, strong-acid, weak-base, continuous, ion-exchange process for nitrate removal from fertilizer plant effluent. HNO_3 and NH_4OH are used as regenerants in that process to produce a NH_4NO_3 brine which is recycled to the NH_4NO_3 fertilizer production plant. The process is not directly applicable to water supply because their nitrate levels were "extremely" high, and no competing anions were mentioned. However, this basic system appears very attractive with respect to regenerant disposal as a soluble, fertilizer by-product which would have relatively low concentrations of the persistent ions: Ca^{++} , Mg^{++} , Na^+ , Cl^- and $\text{SO}_4^{=}$. In addition, a material balance performed on isolated geographic areas where ground water nitrate is a problem would demonstrate that recycling the "old" nitrate as a local fertilizer would lessen the accumulation of nitrate in the local and surrounding ground water and surface water due to a reduction in the input of new fertilizer nitrogen required from outside the area.

The Sirotherm Process: Thermal Regeneration

It has been suggested in a review by Sabadel [61] that the waste disposal problem in nitrate ion exchange might be eliminated by use of thermal rather than chemical regeneration. A thermal regeneration process trade-named Sirotherm has been developed by Weiss et. al. [15, 134] comprising a single-bed exchanger of mixed weak-acid, weak-base resins operated at low (20°C) temperature during the ion-exchange step and at high (80°C) temperature during the regeneration, acid-base elution, step. Since "low-grade heat sources" (under 90°C) are used, the costs of regeneration, and hence the operating costs of the process are said to be nil. However, in 1969, Bregman and

Schackelford [22] pointed out several significant disadvantages of the process:

(1) The ion-exchange kinetics are very slow since the operation takes place at neutral (5 to 7) pH.

(2) The extremely fine particles (5 to 20 microns) which must be used to obtain reasonable ion-exchange rates lead to enormous bed surfaces and very-low flow rates which in turn promote flow distribution problems and prevent rapid heat transfer during regeneration.

(3) Because resin capacity is limited to that arising from the differences in resin pKa's between 20°C and 80°C, capacities of less than 1 meq/gm result as compared to 5-9 meq/gm for these same resins regenerated chemically after being operated at basic or acidic pH's in two-bed systems.

(4) High wastewater-to-product-water flow rates are characteristic of the Sirotherm process due to these low resin capacities and the need for frequent regeneration.

According to Bolto (personal communication and Ref. 15) by 1975 the disadvantages arising from the well-known, slow kinetics for weak resins [6, 14, 61, 62, 76, 134, 135] and very low resin capacities had been largely overcome and several successful 12,000 gpd ($45 \text{ m}^3/\text{day}$) pilot plants (both fixed bed and continuous) had demonstrated the usefulness of the process in partially desalting ground waters containing 1000--2000 ppm TDS. Product water yields were in the 67--91% range with typical TDS reductions of 50--60% while wasting 9--33% of the feed as an 80°C wastewater with 3000 to 5500 ppm TDS. Typical product-to-wastewater flows were 4/1 to 9/1 with more complicated, continuous ion-exchange designs and staged operations being required for the 9/1 ratio. The reported capacities were still quite low (0.12 to 0.20 meq/ml) compared to conventional, chemically regenerated resins (1.0 to 3.0 meq/ml) in the same type of service.

In coastal locations and in semi-arid regions where low-cost

land is available the disposal of large volumes of saline, 80°C water may be accomplished by discharging into the ocean or by evaporation.

For non-coastal, non-arid, nitrate-removal applications, wastewater disposal will be a serious problem. Furthermore, particulates and oxygen must be completely removed prior to Sirotherm desalination. Lastly, the inevitable, accelerated resin deterioration upon repeated cycling to 80°C may cause a serious organics problem in the product water.

No published cost figures are available on the Sirotherm process, but ICI Australia Ltd. a partner in the process development is planning to build a 165,000 gpd ($625 \text{ m}^3/\text{day}$) Sirotherm commercial desalting process at one of their plants [15].

Strong-Base Anion Exchangers: Summary

The previous discussion pertaining to single-bed strong-base anion systems for nitrate removal from water supplies can be summarized as follows:

- (1) Resin selectivity for nitrate is a serious problem because sulfate is preferred with a selectivity ratio of over 2/1 at low TDS.
- (2) Ferrous iron, when present, oxidizes, precipitates, and seriously fouls the resin.
- (3) Regeneration and brine disposal are the major economic and environmental problems yet to be solved even with low-cost NaCl regeneration.

THE PROCESS PROPOSED FOR STUDY

Process Description

Because the strong-acid, weak-base process appeared to have

certain advantages with respect to regeneration efficiency, iron removal, regenerant disposal and possibly nitrate selectivity, the little-studied, weak-base resin part of the system shown in Figure 1, following, was studied in detail. The thermodynamic and kinetic results of the work were compared and contrasted to those of a single, strong-base, anion resin in similar nitrate removal service; see Figure 2.

Advantages and Disadvantages of Proposed Process

Evans [47] reported on similar nitrate removal process but with HCl and lime as the regenerants. He pointed out that, even after the cation bed was exhausted, and sodium was being eluted, the system continued to provide softening and nitrate removal thereby delivering greater than stoichiometric efficiency due to the weak-base anion resin's apparent selectivity for nitrate over all the other anions present. Interpreting his published results, this author calculated the following selectivity sequence: $\text{HNO}_3 \gg \text{H}_2\text{CO}_3 > \text{H}_2\text{SO}_4 > \text{HCl}$ which is in obvious contrast to the previously reported sequence of $\text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HCl} \gg \text{H}_2\text{CO}_3$ [36, 60, 78] for both weak and strong base resins. The high selectivity for H_2CO_3 is very weakly held on strong-base resins and is always the first ion to break through in column studies [10, 44, 86]. Further, several sources of published, ion-exchange design information [36, 104] state unequivocally that carbonic acid is not significantly removed by weak-base, anion resins. This very unusual selectivity sequence indicated by Evans' data is most likely due to one or more of the following: (1) true thermodynamic selectivity (2) kinetic selectivity due to non-equilibrium, mass transfer or (3) analytical errors. An explanation based primarily on (1) and (2) above was favored since a weak-base resin with $\text{pK}_a \approx 8$ would certainly have reacted with (adsorbed) H_2CO_3 at low pH (<4) as CO_2 has been shown to be readily stripped from air by weak-base resins [132]. Further, weak-base resins are known to be kine-

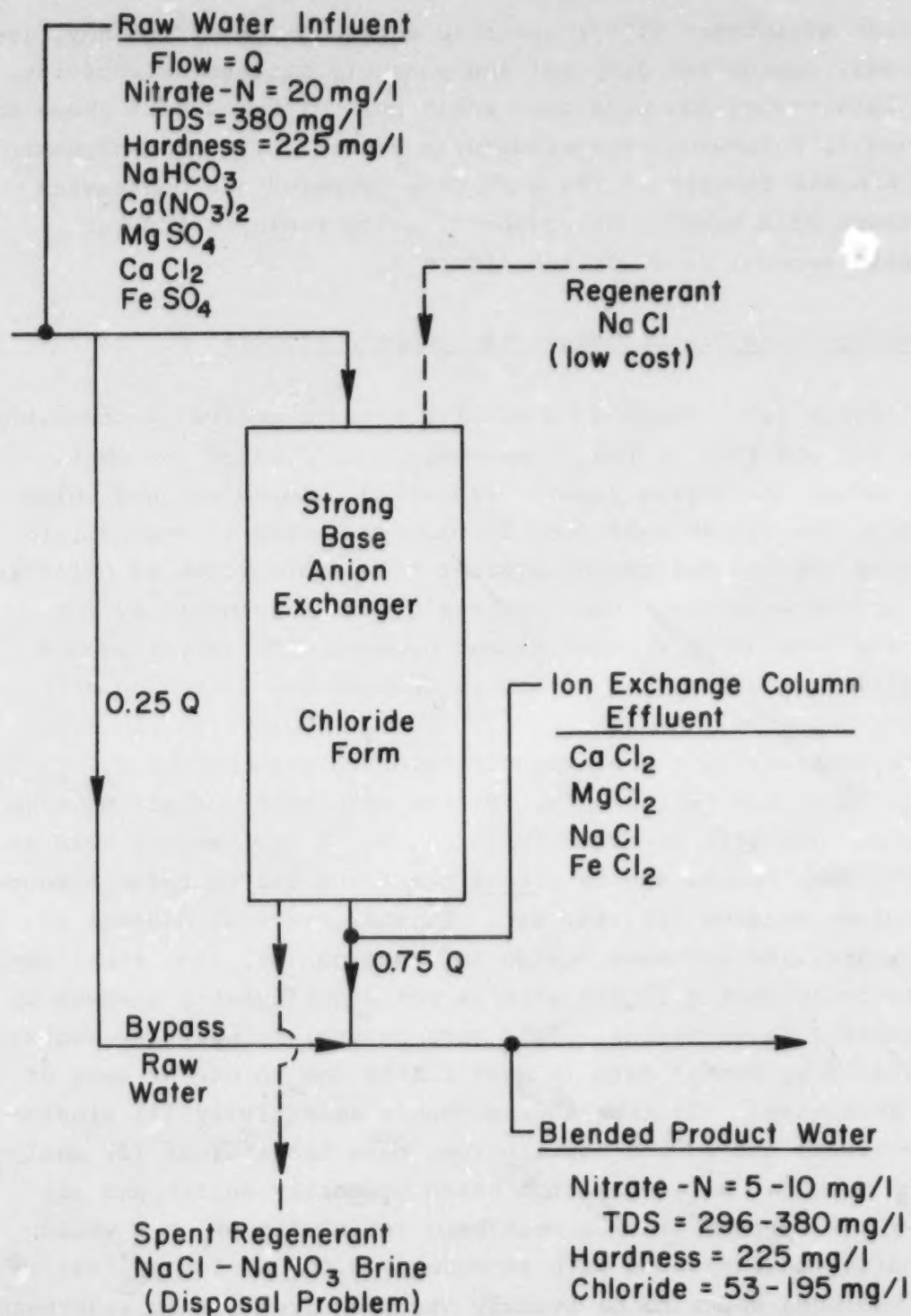


Figure 1 Conventional Single Bed Ion Exchange Process

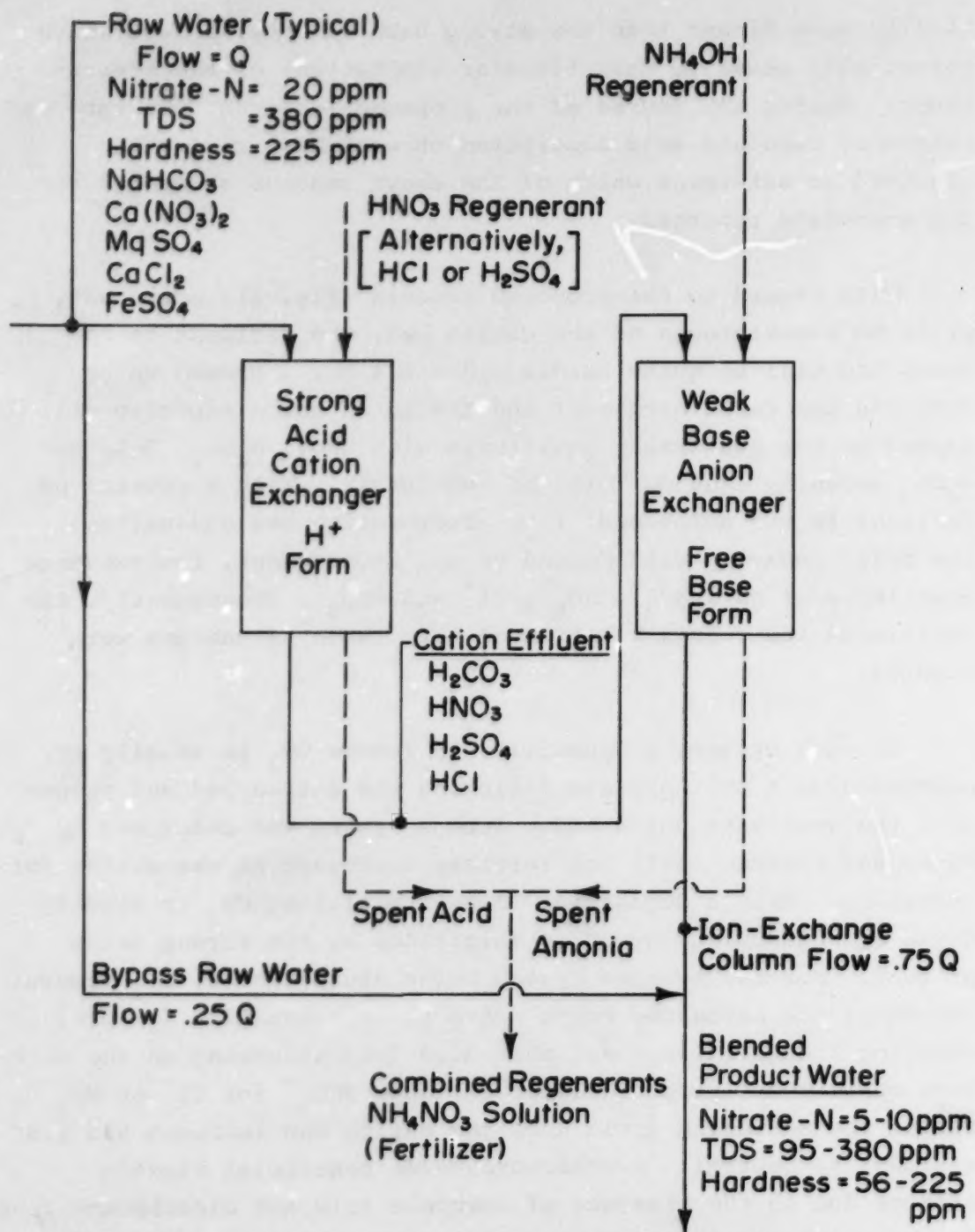


Figure 2 Proposed Two-Bed, Ion-Exchange Process

tically much slower than the strong base variety, a fact which potentially leads to mass transfer limitations of the separations. During the course of the proposed research, the rate and extent of carbonic acid adsorption on weak-base resins was examined to determine which of the above reasons accounted for the anomalies reported.

With regard to the proposed process (Fig. 1), note that, prior to breakthrough of the cation bed, the influent to the anion bed will be quite acidic ($\text{pH} \approx 2.4$ for a ground water with 250 ppm CaCO_3 hardness) and the total anion capacity will depend on the quaternary equilibria with HNO_3 , H_2SO_4 , HCl , and H_2CO_3 assuming that OH^- will be negligible. With a neutral pH influent to the anion bed, i.e. after cation bed exhaustion, the resin capacity will depend on the 5-component, ion-exchange equilibria of OH^- , NO_3^- , SO_4^{2-} , Cl^- and HCO_3^- ; consequently, the equilibria and column kinetics of both these situations were studied.

In such systems a degasifier to remove CO_2 is usually recommended as a unit process following the cation bed and preceding the weak-base anion bed. Such a system was described by Sanks and Kaufman [108] for tertiary treatment of wastewater for recycling. With a degasifier in this position, CO_2 is readily given off because a low pH is maintained by the strong acids present. For the two-bed system being studied here, CO_2 removal preceding the anion bed might prove to be a negative feature; removing H_2CO_3 will prevent that acid from adsorbing on the weak-base resin where it could later exchange HCO_3^- for Cl^- or NO_3^- during the softening cycle when the cation bed is spent and its effluent is neutral. Furthermore, some beneficial kinetic effects due to the presence of carbonic acid and bicarbonate ions in the anion bed influent were also expected (personal communication, I.W. Abrams). For these reasons a degasifier was not used during the experimental work.

Regardless of the efficiency of bicarbonate removal, the added benefits of demineralized water or soft, nitrate-free water tend to offset the cost disadvantages of two-bed systems with their requirements for regeneration and neutralization of two beds rather than one.

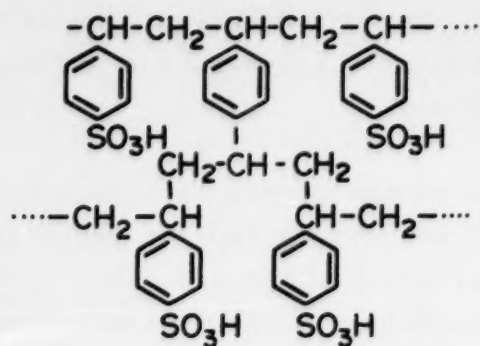
Another feature of the system is bypass blending of the raw water. This feature permits control of the nitrate concentration at values approaching the permissible limit in the blended water supplied to the distribution system. Thus, not all of the raw water needs to be treated; typically one-fourth to one-half of the raw water will bypass the ion-exchange beds.

THE STRUCTURE OF ION-EXCHANGE RESINS

Introduction

A brief description of the chemical and physical structures of at least one representative type of resin from each major classification of synthetic, organic ion exchangers is included here to facilitate the explanation of (1) differences between strong and weak resins, (2) selectivity theory, and (3) kinetic theory.

A Typical Strong-Acid Cation Resin: Duolite C-20



Sulfonated polystyrene-divinylbenzene copolymer

Typical degree of crosslinking: 8%

Physical form: Translucent spheres

Specific gravity: 1.23, hydrogen form

Moisture retention capacity: 50%, hydrogen form

Effective size: 0.45 to 0.55 mm

Swelling: -7% when going from H⁺ to Na⁺ form

Ion-exchange capacity: 4.8 meq/gm, 2.0 meq/ml

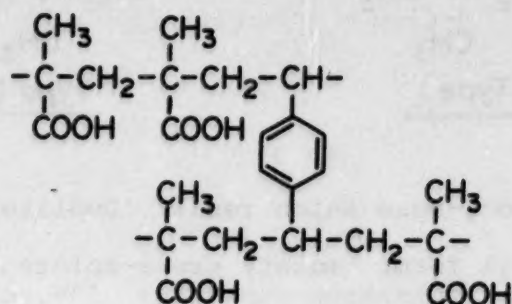
Uniformity coefficient: 1.4 to 1.8

Functional group: R-SO₃H

Acidity: pK_a < 1, ionized at pH > 1



A Weak-Acid Cation Resin



Methacrylic acid-divinylbenzene copolymer

Functional group: COOH

Acidity: $\text{pK}_a \approx 4$ to 6, ionized at $\text{pH} > 5$

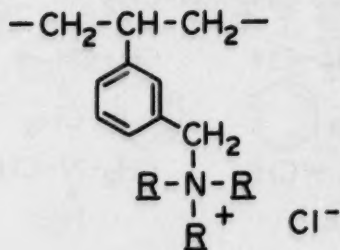
Swelling: +65% going from H^+ to Na^+ form

Capacity: 10 meq/gm, 4.3 meq/gm



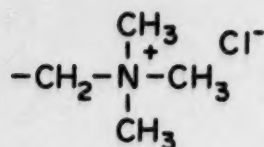
$\overline{\text{R}}$ denotes the resin matrix

Strong-Base Anion Resins

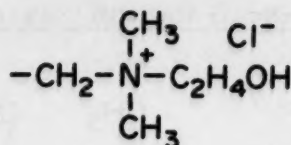


$\underline{\text{R}}$ denotes a methyl or ethanol group

If all the " $\underline{\text{R}}$ " groups are methyl, the resin is a Type 1 Quaternary ammonium resin. Type 2 resins have two methyl and one ethanol group as shown below:



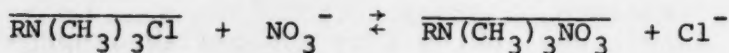
Type 1



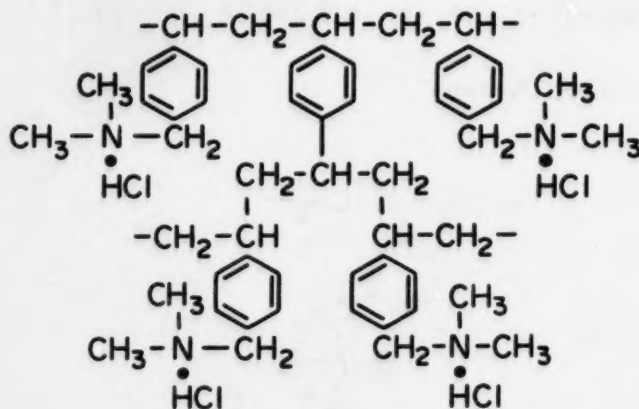
Type 2

Typical Strong-base anion resin: Duolite A-101-D, Type 1

Physical form: moist, cream-colored beads, opaque
 Moisture retention capacity: 50%, chloride form
 Specific gravity: 1.07 chloride form
 Capacity: 4.0 meq/gm, 1.3 meq/ml
 Swelling: -12% going from OH⁻ to Cl⁻ form



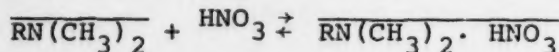
Weak-Base Anion Resins

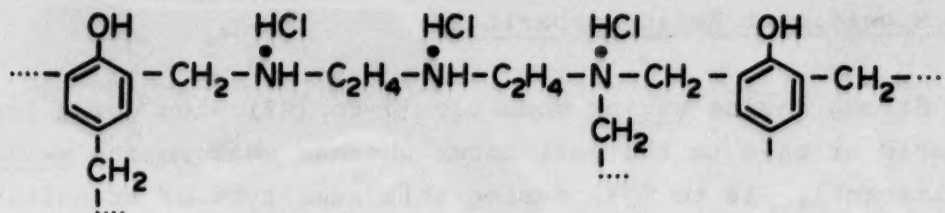


Styrene-divinylbenzene copolymer with tertiary-amine functionality

Typical examples: Amberlite IRA-93, Duolite ES-368

Physical form: tan, spherical particles
 Moisture retention: 50%, free base form
 Capacity: 3.8 meq/gm, 1.3 meq/ml
 Swelling: +23% free base to salt form
 Basicity: pK_a ≈ 7 to 9, ionized at pH < 8





Phenol-formaldehyde polyamine, condensation polymer with secondary amine functionality

Typical example: Duolite A-7

Physical form: cream colored granules

Specific gravity: 1.12, free base form

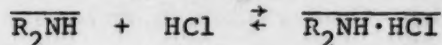
Particle size: 0.3 to 1.2 mm

Moisture retention: 60%

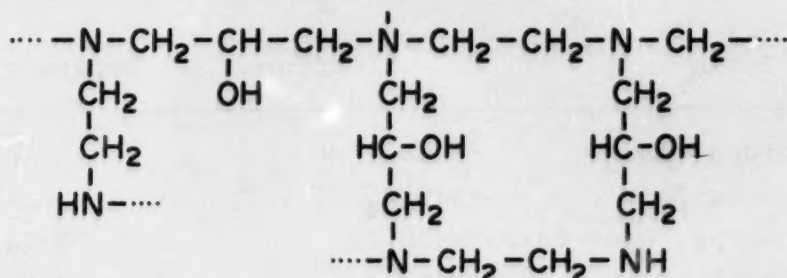
Total capacity: 9.1 meq/gm, 2.4 meq/ml

Swelling: +18% going from free base to salt form

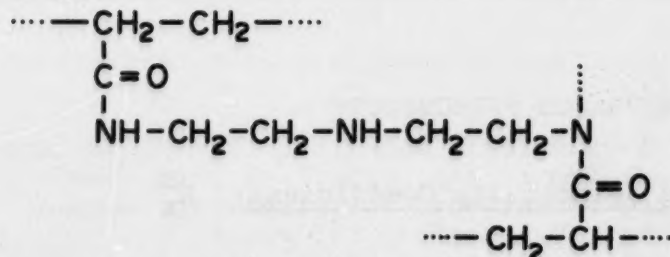
Basicity: $\text{pK}_a \approx 7$ to 9, ionized at $\text{pH} < 8$



Other Common Weak-Base Resins



Epoxy-polyamine condensation polymer



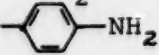
Polyacrylic-polyamine copolymer

Some Significant Resin Comparisons

Strong resins shrink modestly (7 to 12%) when going from the acid or base to the salt forms whereas weak resins swell significantly (18 to 65%) during this same type of transition. Shrinking denotes a thermodynamic preference for the shrunken state in agreement with the high selectivities observed for the hydrogen and free-base forms of weak-acid and weak-base resins respectively.

Table 1 summarizes the pK_a 's associated with various functional groups. Note that the capacity of a weak base resin is significant only at pH's below the listed pK_a i.e. weak-base resins won't "split neutral salts" to a significant extent. The resins will first adsorb acids then exchange anions.

TABLE 1. SUMMARY pK_a 's FOR ANION RESINS [60]

Resin	Structure	Apparent pK_a
Type 1, Strong-Base	$-N(CH_3)_3OH$	> 13
Type 2, Strong-Base	$-N(C_2H_4OH)(CH_3)_2OH$	> 13
Secondary Amine, Weak-Base	$-N(CH_3)H$	7 to 9
Tertiary Amine, Weak-Base	$-N(CH_2)_2$	7 to 9
Primary Amine, Weak-Base	$-NH_2$	7 to 9
Phenylamine, Weak-Base		5 to 6

THEORIES OF ION-EXCHANGE SELECTIVITY

Definition of the Selectivity Coefficient: K_A^B

Utilizing Donan membrane equilibrium theory [9], the law of mass action [103], or Langmuir isotherms [18], one arrives at an

equilibrium expression which is the same for all three. Consider the general ion-exchange reaction:



$\pm a \pm b$ = valence of ion

R = resin

$\bar{A}$ = overbar denotes resin phase

Choosing the hypothetical state of unit activity for infinitely dilute solution of both ions in both phases, the following expression results at equilibrium:

$$\frac{ac_{\overline{B}}^{|a|} ac_{\overline{A}}^{|b|}}{ac_B^{|a|} ac_{\overline{A}}^{|b|}} = 1 = \frac{q_B^{|a|} C_A^{|b|}}{C_B^{|a|} q_A^{|b|}} * \frac{\gamma_{\overline{B}}^{|a|} \gamma_{\overline{A}}^{|b|}}{\gamma_B^{|a|} \gamma_{\overline{A}}^{|b|}}$$

$ac_{\overline{B}}$ = activity of B in the resin phase

ac_B = activity of B in the solution phase

$\gamma_{\overline{B}}$ = activity coefficient of B in the resin

γ_B = activity coefficient of B in the solution

q = resin phase concentration

C = solution phase concentration

The Selectivity coefficient, K_A^B has been defined as: [60]

$$K_A^B = \left[\frac{q_B}{C_B} \right]^{|a|} / \left[\frac{q_A}{C_A} \right]^{|b|} \quad (3)$$

Interpreted in terms of activity coefficients:

$$K_A^B = \left[\frac{\gamma_B}{\gamma_{\overline{B}}} \right]^{|a|} \left[\frac{\gamma_{\overline{A}}}{\gamma_A} \right]^{|b|} = \frac{\gamma_{\overline{B}}^{|a|} \gamma_{\overline{A}}^{|b|}}{\gamma_B^{|a|} \gamma_{\overline{A}}^{|b|}} \quad (4)$$

Usually, in dilute solutions $\gamma_A \approx \gamma_B \approx 1.0$ so that the selectivity coefficient is determined by the activities of the respective ions in the

resin phase only:

$$K_A^B \approx \frac{\sqrt{b|}}{\sqrt{a|}} = K_A^{B'} \quad K_A^{B'} = \begin{matrix} \text{solution-phase} \\ \text{corrected selectivity} \\ \text{coefficient} \end{matrix} \quad (5)$$

It is important to note that K_A^B is a coefficient and is not necessarily constant as the activities of the ions in the very concentrated resin phase tend to depend on the ratio of the concentrations present. Generally, K_A^B decreases as y_B (the equivalent fraction of B in the resin) increased [103].

The Separation Factor: α_A^B

The widely accepted definition for the parameter describing partitioning of solutes between two phases is:

$$\alpha_A^B = \frac{q_B/C_B}{q_A/C_A} \quad (6)$$

For monovalent ion exchange then:

$$\alpha_A^B = K_A^B = \frac{q_B}{C_B} \frac{C_A}{q_A} = \frac{y_B}{x_B} \frac{x_A}{y_A} \quad (7)$$

where:

y_A = Equivalent fraction of A in resin phase

x_A = Equivalent fraction of A in solution phase

For univalent-divalent exchange $\alpha_A^B \neq K_A^B$. Since the separation factor doesn't include the stoichiometric coefficients as exponents, it's a mathematically and physically more satisfying description of solute distribution even though it is also not usually a constant. See Appendix 5, Justification of α_j^i .

The Concept of Electroselectivity [60, 103]

Consider the case of $\text{SO}_4^{=}/\text{NO}_3^-$ ion exchange in dilute

(0.010 N.) aqueous solution where $C_N = C_S = 0.005$ N.:



$$K_A^B = K_N^S = \left[\frac{q_S}{C_S} \right] \left[\frac{C_N}{q_N} \right]^2 = \left[\frac{C_0}{Q} \right] \left[\frac{y_S}{x_S} \right] \left[\frac{x_N}{y_N} \right]^2 \quad (9)$$

C_0 = Total solution concentration, meq/ml

Q = Resin exchange capacity, meq/gm

Theoretically (and actually), this selectivity coefficient is a function of the total solution concentration C_0 (which is not the case in univalent-univalent or divalent-divalent exchange). Now, if we further assume that the resin has no "selectivity" i.e., $K_N^S = 1$, this does not imply an inability to separate SO_4^{2-} from NO_3^- . For example, if $Q = 8$ meq/gm (a typical value), the calculated separation factor ≈ 50 , i.e., the resin phase contains 50 times as many equivalents of sulfate as nitrate. This theoretical ability to separate multivalent ions has been termed "electroselectivity" [60], and has been found to be a fair approximation for cation exchange. For strong-base anion exchange in this range of concentration however, α_N^S has been found to be more like 2.5 not 50. So, here, Donan membrane equilibrium and mass-action derivations which assume nearly equal resin-phase, activity coefficients are poor approximations. This was thought to be fortunate since we intuitively desired that α_N^S be as low as possible. To that end, the equilibrium of sulfate and nitrate with a large number of strong and weak-base anion resins was studied. It will be shown later that the intuition about the sulfate/nitrate selectivity being the most important selectivity was incorrect.

As a final comment, it can be shown that this electroselectivity preference for the multiply-charged ion becomes greater with increasing dilution of the external solution. Conversely,

at high solution concentration, the electroselectivity diminishes, and in some cases, e.g. $\text{SO}_4^{=}/\text{Cl}^-$ at $C_T \geq 0.063$ N and $\text{SO}_4^{=}/\text{NO}_3^-$ at $C_T \geq 0.050$ N, inverts in favor of the monovalent ion. See Refs. 77 and 10 respectively.

Binary Isotherms

Having chosen the separation factor for description of anion equilibria, it should be noted that even if α_A^B is a constant, linearity of the isotherm plot of a y_A vs. x_A is not implied. In fact, the Langmuir, multicomponent equilibrium treatment leads to $\alpha_A^B = \text{constant}$; for example;

$$q_A = \frac{Q' b_A C_A}{1 + b_A C_A + b_B C_B} \quad (10)$$

$$q_B = \frac{Q' b_B C_B}{1 + b_A C_A + b_B C_B} \quad (11)$$

$$\alpha_A^B = \frac{q_B C_A}{q_A C_B} = \frac{b_B}{b_A} = \text{constant} \quad (12)$$

Q = Langmuir ultimate solid-phase adsorption (or ion exchange) capacity

b_i = Langmuir constant related to adsorption (or ion exchange) energy

Figure 3 below illustrates constant and variable separation factor isotherms:

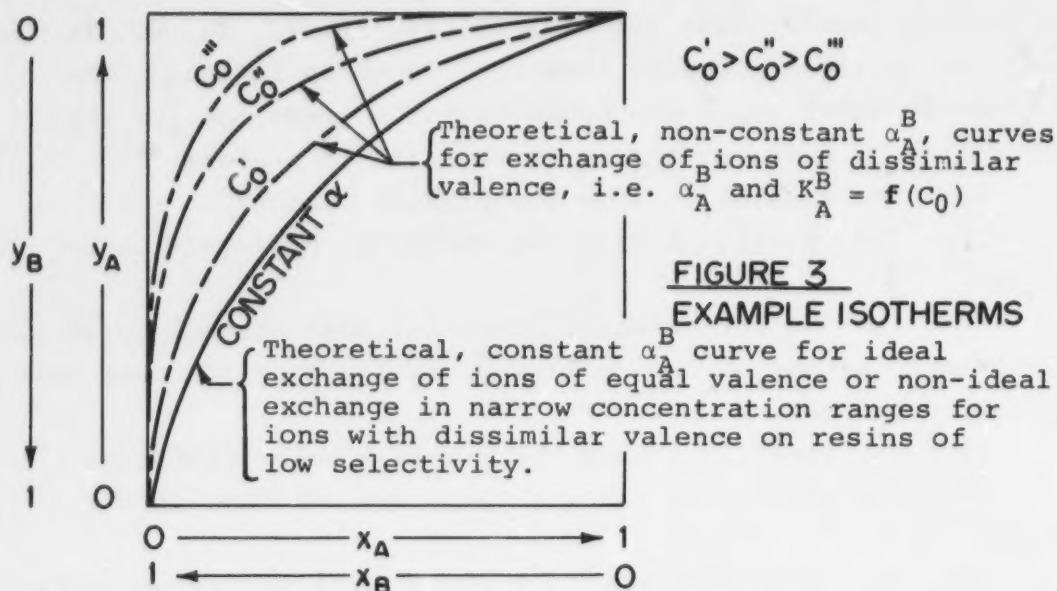
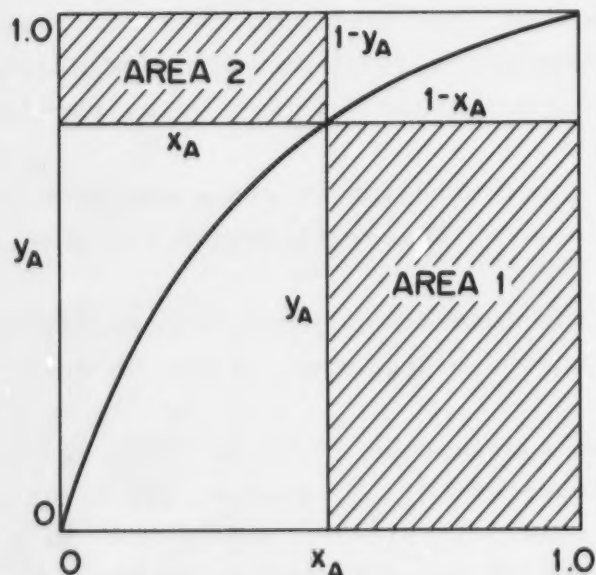


FIGURE 3
EXAMPLE ISOTHERMS

Figure 4 below demonstrates that the binary separation factor α_B^A is equivalent to the ratio of the area 1 and 2.



$$\alpha_B^A = \frac{(y_A)(1-x_A)}{(1-y_A)(x_A)}$$

$$\alpha_B^A = \frac{\text{Area 1}}{\text{Area 2}}$$

FIGURE 4
ISOTHERM AREAS

General Considerations Regarding Selectivity

As a result of much theoretical speculation and some experimental verification [21, 18, 20, 26, 39, 40, 43, 60, 86, 103, 113] the following factors have been found to influence the preference which any resin exhibits for a given ion (or ions). The cation or anion exchanger is reported to prefer:

- (1) The counterion with the highest valence.
- (2) The counterion with the smallest, hydrated-ionic radius.
- (3) The counterion which interacts most strongly with the fixed ionic groups on the resin (especially true for weak-acid or weak-base resins).
- (4) The counterion with the greatest polarizability.
- (5) The counterion causing the least swelling of the resin.
- (6) The counterion with the lowest free energy of hydration in aqueous solution.

Rules (1) and (2) can be applied without exception to the alkali and alkaline earth cations, in fact it is from experiments with these cations that the rules were derived. However, anion exchange is not exactly analogous to strong-acid cation exchange, the following important differences being relevant to the research done here.

(1) The charge on the counterion in anion exchange has much less effect on selectivity than with cation exchange [39, 113].

(2) The nature of the functional group, especially its size and charge density have a significant effect on anion selectivity [13].

(3) When going from strong-base $-N(CH_3)_3^+$, quarernary ammonium groups to weak-base $-N(CH_3)_2H^+$ groups, the selectivity sequence for the halide ions: $I > Br > F^-$ (1000 > 150 > 5) remains unchanged but the magnitude of the differences is reduced mark-

edly (100 40 10). See figures 4-2 and 4-3 from reference [39]. On this basis it was expected that the selectivity sequence $\text{SO}_4^- > \text{NO}_3^- > \text{Cl}^-$ would be the same with weak-base resins but with smaller absolute differences in selectivity values. Generally this was not found to be true.

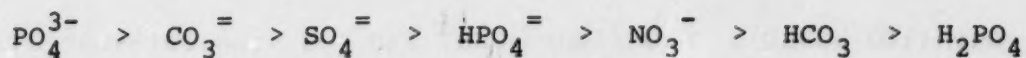
(4) The hydrated ionic radius is not necessarily the most important factor in anion exchange selectivities. In fact, Reichenberg [103] argues that this "apparent correlation" between selectivity and hydrated ionic radius is an "unfortunate accident" and that the true causal relationship is due to the free energy of hydration i.e., selectivity is inversely proportional to this energy. (See also Eisemen) [43]. As an example of this he cites the well-known selectivity sequence of $\text{ClO}_4^- > \text{I}^- > \text{Br}^- > \text{Cl}^-$ on strong-base resins with ClO_4^- being preferred to Cl^- by more than 100/1. Based on hydrated ionic radius the sequence should be $\text{Br}^- > \text{I}^- > \text{Cl}^- > \text{ClO}_4^-$. However, based on anionic-hydration enthalpy the correct sequence is predicted. It is interesting to note that HClO_4 is also much preferred to HCl during adsorption from aqueous solution onto activated, coconut-shell carbon [112] probably for the same reason as with synthetic organic resins.

In this same vein, Midkiff [50] in what appears to be a rather bold departure from the accepted hydrated ionic radius theories, had a good degree of success in correlating selectivity to ionic valence and crystal ionic radius. The basic equation which he applied to polyatomic-anion exchange on strong-base resin in dilute aqueous solution is:

$$(13) \quad K_A^B \propto \frac{Z}{R_I}$$

Z = valence
 R_I = crystal ionic radius
 $\propto$ = indicates proportionality

The selectivity sequence predicted by the above equation was calculated as:



His experimentally observed selectivity sequence was nearly as predicted with the position of $\text{CO}_3^{=}$ being the only notable exception, i.e.,



Careful examination of the actual relationship between hydrated ionic radii and his calculated, crystal ionic radii (using the accepted criterion of ionic conductance being inversely proportional to hydrated ionic radius) discloses that the inverse relationship expected, based on observations of the alkali and alkaline earth metal cations completely fails with the polyatomic anions studied. This is to say that hydrated ionic radius is not inversely proportional to crystal ionic radius as it is with cations, but directly proportional to it, and that explains why the prediction was so good. So, the rule-of-thumb stating that selectivity is inversely proportional to hydrated ionic radius still applies (except for $\text{CO}_3^{=}$) in the specific system described.

Summary of Selectivity Considerations

Based on published data [10, 36, 60, 78, 113] the selectivity (and separation factor) sequence expected for strong-base ion exchange with the anions of interest is:



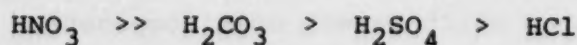
No single criterion such as limiting ionic conductance, free energy of hydration, valence or combination of valence and radius can be used to correctly predict the entire sequence even in the simplest of systems. Part of the intended research effort was aimed at verifying and quantifying the above sequence for ground waters in equilibrium with the most nitrate selective strong-base

resins.

For weak-base resins, the sequence based on published data [18, 60, 78] is essentially the same as above:



However, it must be observed that prior to the research reported here no useful systematic treatment of weak-base resin equilibria could be found in the literature, thus the above sequence was originally viewed only as a guide although it was later verified. It is to be noted that HNO_2 is absent completely due to lack of any published data. Finally, recalling the earlier discussion of Evans' experimental results where the calculated sequence was (surprisingly)



it was concluded that a systematic experimental treatment of weak-base equilibria needed to be undertaken to resolve the problem as the actual sequence would determine the nitrate ion-exchange capacity in chromatographic elution service.

MULTICOMPONENT EQUILIBRIUM THEORY

Batch Equilibrium Studies

Based on the preceeding discussion, it may reasonably be concluded that there is no point in dealing with predictive equations based on thermodynamic considerations for multicomponent equilibria when binary selectivities can't even be correctly predicted.

Some encouraging evidence that experimental, binary equili-

Equilibrium data might be applied to batch systems of variable total concentration with three or more components was presented by Peroni and Dranoff [99]. They determined that single-valued, binary selectivity coefficients could be used to describe Cu^{++} , Na^+ , H^+ equilibria with strong-acid resins in the concentration range of 0.01 to 0.10 N. For the experiments performed in our work, it was expected that the binary separation factors would be reasonably constant because of the narrow range (0.002 -- 0.008 N) of variation of the individual and total concentrations.

Column Equilibrium Studies

If the binary separation factors are reasonably constant, the specialized multicomponent equilibrium theories for ion exchange and chromatographic separations may be applied [27, 63, 64, 71, 119]. The relevant mass balances and equilibrium expressions for ion-exchange columns which permit multicomponent concentration profiles to be predicted from constant separation factors at a constant total solution concentration are:

$$\alpha_{ij}^i = \frac{y_i x_j}{x_i y_j} \quad (14)$$

n = number of components

k = an arbitrary component

$$\sum_i x_i = 1 \quad (15) \quad i = \text{component number 1}$$

j = component number 2

$$\sum_i y_i = 1 \quad (16)$$

$$x_i = \frac{x_i}{\sum_j \alpha_{ij}^i y_j} = \frac{\alpha_{ik}^k y_i}{\sum_j \alpha_{ij}^k y_j} \quad (17)$$

$$y_i = \frac{x_i}{\sum_j \alpha_{ij}^j x_j} = \frac{\alpha_{ik}^i x_i}{\sum_j \alpha_{kj}^j x_j} \quad (18)$$

and the affinity sequence is

$$i > j > k > l \dots > n$$

so that $\alpha_j^i > 1$; $\alpha_k^j > 1$, etc.

Klein, Tondeur and Vermeulen [71] have demonstrated that by using these relationships in conjunction with integral and differential material balances, the concentration profiles of each component in either the resin or liquid phase can be determined in ion-exchange columns under equilibrium conditions. In representing the column concentration profiles and in writing the differential balances, the dimensionless throughput parameter "T" is utilized:

$$T = \frac{C_0 (V - v\epsilon)}{1000 vQ} = \text{Throughput} \quad (19)$$

$$T = \frac{\text{Total meq of ions fed to the column}}{\text{Total meq of column ion-exchange capacity}}$$

where:

- C_0 = Constant total solution conc., meq/l
- Q = Resin capacity, meq/ml
- ϵ = Column void fraction, dimensionless
- V = Feed solution volume, l
- v = Resin bed volume, l

Their mathematical development leads to the following rules governing equilibrium column profiles:

- (1) The number of plateau zones is equal to the number of components in the system.
- (2) Between each plateau zone is a transition zone which may be either abrupt or gradual depending upon whether a boundary is self-sharpening or non-self-sharpening.
- (3) The "root," "alphabet," and "slope" reuls [71] may be utilized to further define the shapes and locations of these transition zones.

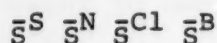
Analytical solutions are presented by Tondeur and Klein

[119], Helfferich and Klein [64] and Helfferich [63] for the set of integral and differential mass balances in the constant separation factor case for any number of components. The more general case of constant selectivity coefficients may be solved by numerical methods [71]. Unfortunately, all of the above solutions assume a constant total solution concentration ($C_0 = C_T$) which is a very good approximation for pure ion-exchange without neutralization. For example, it applies to strong-base exchange of Cl^- for NO_3^- but not to activated carbon adsorption processes or to the second bed in a two-bed ion-exchange system where molecular adsorption or ion exchange with neutralization occurs causing C_T to approach zero upon continuous contact with the solid phase. Helfferich [64] has termed this "non-stoichiometric sorption" and suggests the creation of a dummy species whose concentration makes up for the difference between the variable C_T and some mathematical constant, e.g., C_0 , the total initial solution concentration in the column feed. How the concept is applied to the analytical solution of constant separation factor column equilibria is discussed in detail in Reference 64, pp. 283-298.

If we accept the published selectivity sequence:

sulfate > nitrate > chloride > bicarbonate

as being true for the proposed process of weak-base anion exchange with an acidic influent to a non-presaturated bed then Helfferich's "unique pattern" rules for column profiles [60, pp. 163-4] may be applied if some further assumptions are made, viz., (1) that the dummy species created has a lower affinity than all real species, (2) that sufficient time has passed for coherent boundaries (i.e., stable traveling loci of constant composition) to have developed and (3) that the resin-phase capacity is constant. In this "unique" case the solid-phase profile can be represented as



where $\bar{S}$ denotes an abrupt boundary in the resin phase which

separates an upstream zone containing the superscripted anion from downstream zones in which that particular anion is absent. The profile is, of course, read from left to right. Applying that rule to the case in point, i.e., nitrate removal from groundwater in the presence of the competing anions sulfate, nitrate, and chloride results in the idealized resin phase concentration profile shown below in Fig. 5.

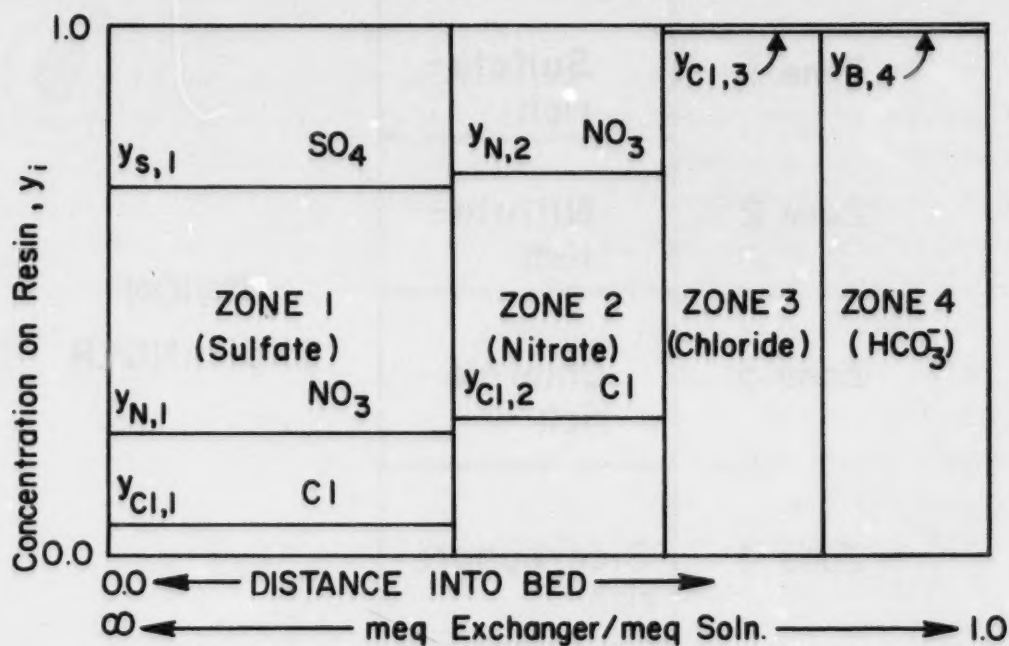


FIGURE 5

HYPOTHETICAL RESIN PHASE CONCENTRATION PROFILE

$y_{Cl,i}$ = eq. fraction of chloride in zone i

$y_{s,1}$ = eq. fraction of sulfate in zone 1

$y_{N,1}$ = eq. fraction of nitrate in zone 1

$y_{N,2}$ = eq. fraction of nitrate in zone 2

$y_{B,4}$ = eq. fraction of bicarbonate in zone 4

Figure 6 below is a more simplified presentation of Figure 5. It illustrates how a mixture of the four typical ground water anions is partially separated in an exhausted ion exchanger. The first zone is enriched with the most preferred species, the second zone with the second-most preferred species and so on.

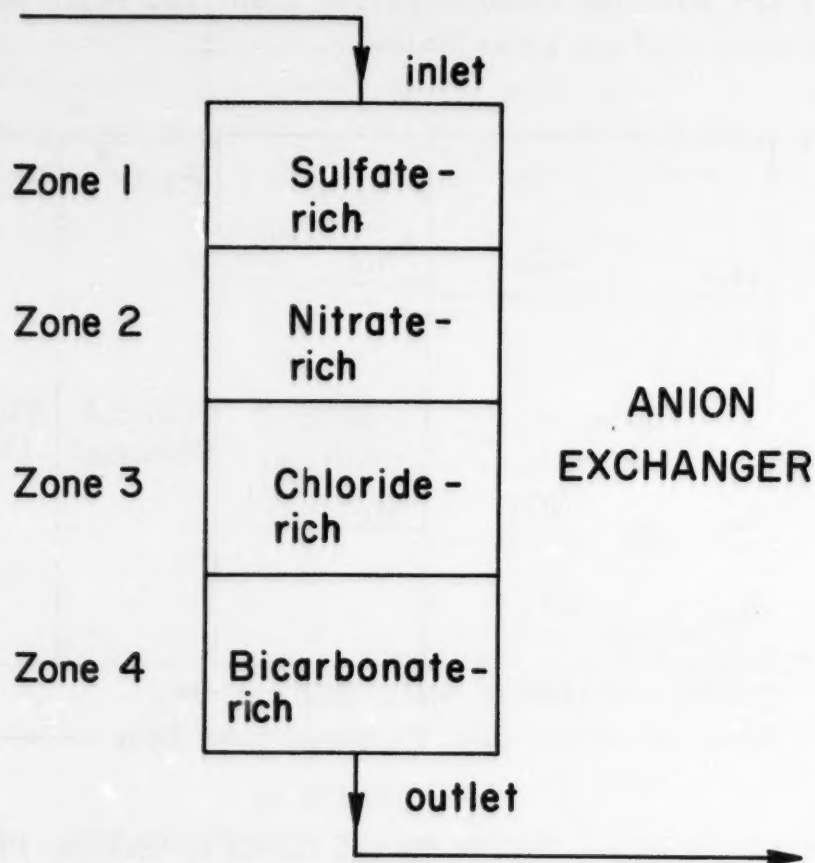


FIGURE 6

Chromatographic Enrichment of Ground
Water Anions in an Exhausted Anion
Exchanger

Knowing the shapes of the zones and assuming constant separation factors, the y_i 's of all species may be calculated assuming that the column is run to nitrate breakthrough. It was expected that problems would undoubtedly arise from the non-validity of the simplifying assumptions especially the conditions of equilibrium and constant capacity which are known not to be true for the kinetically slow, variable capacity weak-base resins. Nevertheless a simplified procedure was developed which did closely predict $\bar{y}_N$ the average equivalent fraction of nitrate on the resin at nitrate breakthrough.

SECTION 5

PHASE I: ANION RESIN SELECTIVITY STUDY

OBJECTIVES:

To determine the sulfate/nitrate selectivities of the commercially available anion resins which might be used in nitrate removal service on groundwaters with total concentrations in the range of 0.002 to 0.008 N.

To determine the nitrate/chloride and nitrate/bicarbonate selectivities of these resins.

To characterize the capacities of all the weak base resins for HCl , HNO_3 and H_2SO_4 as a function of pH, i.e. to determine their titration behavior with these acids.

To establish which resin characteristics are associated with the various selectivities and, hopefully, to determine which physically and chemically controllable resin characteristics are causative of the sulfate, nitrate, chloride and bicarbonate selectivities.

To provide a complete descriptive data base on the various resins which may be used to help predict their column performances in nitrate removal service.

PROCEDURAL OUTLINE: ANION RESIN SELECTIVITY STUDY

(1) Obtain a representative selection of strong and weak base anion resin samples. One pint or one liter samples of the

following resins were obtained from the four U.S. resin manufacturers listed in Appendix D.

TABLE 2. ANION RESIN SAMPLES OBTAINED FOR STUDY
(U-M RESIN NUMBER ASSIGNED FOR THIS STUDY)

Weak Base Resins	Strong Base Resins
(1) Amberlite IRA-93	(14) Amberlite IRA-910
(2) Amberlite IRA-68	(15) Amberlite IRA-400
(3) Amberlite IR-45	(16) Amberlite IRA-402
(4) Dowex WGR	(17) Amberlite IRA-900
(5) Dowex MWA-1	(18) Amberlite IRA-410
(6) Duolite A-7	(19) Dowex SBR-P
(7) Duolite A-340	(20) Dowex SAR
(8) Duolite ES-368	(21) Dowex SBR
(9) Duolite ES-561	(22) Dowex 11
(10) Duolite ES-374	(23) Duolite A-102-D
(11) Ionac A-260	(24) Duolite A-101-D
(12) Ionac AFP-329	(25) Duolite A-104
(13) Ionac A-305	(26) Ionac A-550
	(27) Ionac ASB-1
	(28) Ionac A-641
	(29) Ionac ASB-2
	(30) Ionac ASB-1P
	(31) Ionac A-540
	(32) AFP-100

(2) "Condition" each of the resin samples. Six 2" dia. by 5' high glass columns were used to prepare the resins for further testing by running them through two acid-base cycles with backwashes and intermediate and final distilled water rinses. See Appendix D Procedure D1 for further details.

(3) Convert resins to appropriate ionic forms at 0.002, 0.005 or 0.008 N for determination of selectivities. Samples of

each of the resins were converted to the nitrate and chloride forms prior to determining capacities and establishing isotherm behaviors. See Appendix D (Procedures D2 and D6) for conversion and capacity determination procedures.

(4) For each isotherm point, equilibrate a predetermined, known weight of one of the various forms (e.g. nitrate form) of one of the resins with a measured amount of 0.005 N acid (e.g. 100 ml of H_2SO_4) and analyze equilibrated supernatant for the anions of interest (e.g. NO_3^- and $\text{SO}_4^{=}$) before calculating the relevant x_i and y_i . See Appendix: Procedure D-3 and calculation E-2.

(5) Construct sulfate/nitrate and chloride/nitrate isotherms for the resins. See Appendix A for all the isotherms plots.

(6) Equilibrate, in a closed columnar system, various mixtures of HNO_3 and H_2CO_3 and analyze the column regenerants to determine the bicarbonate/nitrate selectivities of all the weak base resins. See Appendix: procedure D-4 and Figure D4.

(7) Construct H_2SO_4 , HCl and HNO_3 titration curves for each of the weak base anion resins by equilibrating a known weight of resin with a measured amount of acid before determining aqueous phase pH. See Appendix B: Figures B1 thru B12, and Appendix D: procedure D5.

(8) Calculate approximate pK_a 's of resins. pK_a 's were determined by the method outlined by Helfferich (Ref. 60, pp. 84-88).

(9) Make visual observations and judgements from isotherm plots before plotting comparison isotherms.

(10) Calculate average separation factors. See discussion following and Appendix: Calculation E3.

(11) Plot composite isotherms for resins with similar matrices and functional groups. See Figs. 12 thru 17.

(12) Plot comparison isotherms to illustrate effects of matrix and functionality. See Figs. 20 thru 23.

(13) Assemble experimental and published data into a data-

file for statistical analysis by MIDAS. See Tables 3 and F1.

(14) Do preliminary correlations, analyses of variance, scatter plots and regressions.

(15) Create dummy variables to convert matrix and functionality into analytical variables.

(16) Correlate analytical variables. See Tables 5, 6, F2 and F6.

(17) Perform analyses of variance to establish significant influences of categorical variables on selectivities: α_N^S and α_{Cl}^N . See Tables 9 and 10.

(18) Do linear regression analyses and make scatter plots of selected stratifications of the analytical variables. See Figures 7 - 11 and F1 - F10.

(19) Perform multiple regression analyses and selection of regression analyses (optimization) to establish the selectivities, α_N^S and α_{Cl}^N , as functions of the independent analytical variables. See Appendix F for examples of selection of regression output.

(20) Attempt to explain the statistically significant relationships in terms of accepted physiochemical phenomena. See "Results of Statistical Analyses" and "Phase I Results Summary".

(21) Summarize with predictive equations and tables the most important factors determining α_N^S and α_{Cl}^N . See equations 37-43 and Tables 17 and 18.

Visual Interpretations of Isotherms Graphical Representation of Selectivity

Binary sulfate/nitrate isotherms were constructed for all 32 resins and are represented as the upper curves in Figures A1-A32. For 19 of the 32 resins, nitrate/chloride isotherms are represented as the lower curves on the same graphs. To avoid confusion, the reader should keep in mind that each isotherm is binary at a total concentration of 0.005 N and that the exchange taking place is always between nitrate and either chloride or sulfate. Observe that all the sulfate/nitrate isotherms

are favorable for sulfate(convex) whereas all the chloride/nitrate isotherms are unfavorable for chloride (concave). This generally is the expected result and gives rise to the following selectivity sequence for all resins:

Sulfate > Nitrate > Chloride > Bicarbonate

Although bicarbonate and carbonic acid are not represented in any of the isotherms, it was determined, as will be discussed in the following section on bicarbonate/nitrate isotherms, that all resins showed negligible preference for these species.

Sulfate/Nitrate Isotherms

A rapid visual scanning of all the sulfate/nitrate isotherms indicates that there is an extreme range of sulfate selectivity. It appears that the styrene-DVB resins with tertiary amine functionality (resins 1, 5, 8 and 12) or with quaternary amine functionality (resins 14-32) have moderate sulfate preference. Resins with other than Styrene-DVB matrices (Resins 2, 4, 6, 7, 9, 10, 11, and 13) have high to extremely high sulfate preference over nitrate as evidenced by the very convex curvature of the isotherms. One styrene-DVB resin (Resin 3) with polyamine functionality has a high sulfate selectivity compared to the other styrene-DVB resins with tertiary and quaternary amine functionality (resins 14-32). Among the non-styrene-DVB resins (Resins 2, 4, 6, 7, 9, 10, 11, and 13) one resin appears to have significantly lower sulfate selectivity than any of the others. That is Resin No. 2, and it differs from these others which are polyfunctional in that it is monofunctional (tertiary) as advertised and as verified by its experimentally determined titration curve (Fig. B2).

Chloride/Nitrate Isotherms

The range of chloride/nitrate selectivity differences among resins was not nearly so apparent as was the case with sulfate selectivity. It does appear though that the styrene-DVB resins especially those with tertiary amine functionality (Resins 1, 5, 8 and 12) have greater preferences for nitrate as indicated by very concave isotherms than do the others. The epoxy-amine polyamine resins (Nos. 4 and 7) appear to have the least preference for nitrate over chloride, i.e., their isotherms are the least concave. This, of course, an undesirable situation for resins in nitrate removal service.

Bicarbonate/Nitrate Isotherms

There are no bicarbonate/nitrate isotherms. Bicarbonate wasn't measurably taken up as H_2CO_3 . Nine weak-base resins (Nos. 1-6 and 8-10) and three strong-base resins were chosen for the initial bicarbonate/nitrate selectivity screening. Considerable effort was expended developing a dynamic procedure in which solutions containing various ratios of $\text{HCO}_3^-/\text{NO}_3^-$ sodium salts were decationized in a large (100 ml of resin) cation column followed by 12 small (2 ml of resin) anion columns each containing a 1.00 meq. sample of one of the resins; see Bicarbonate Selectivity Determination Procedure, Appendix A. Following exhaustion of the anion resins they were regenerated with NH_4OH or NaOH and the regenerants analyzed for HCO_3^- and NO_3^- . As one might have expected at the low solution phase pH's existing in these studies (2.4 to 3.0), the uncharged H_2CO_3 molecule did not appear to have participated to any significant extent in ion exchange in either the strong base or weak base resins. The conclusion then, which is applicable to our proposed nitrate removal system, is that no significant, net HCO_3^- removal can be expected anywhere in a weak base anion column where the pH is 3.0 or less. That however doesn't completely preclude

HCO_3^- removal since the lower reaches of an unexhausted bed will be near neutral in pH as will the entire bed during its exposure to the near neutral effluent from an exhausted cation bed. Furthermore, results of the bicarbonate selectivity determination indicated that H_2CO_3 and probably HCO_3^- are catalytic for the eventual removal of the more preferred species: chloride, nitrate and sulfate in columnar, ion-exchange processes.

Generalizations from the Observations

High sulfate selectivity is associated with non-styrene-DVB matrices and polyamine functionality and this should be considered in choosing either a weak or strong base resin for nitrate-ion removal in the presence of sulfate. Note that with these particular resins the avoidance of polyamine functionality is equivalent to the rejection of resins with mixed, secondary and tertiary functional groups as those are the major constituents of polyamine resins. To minimize sulfate selectivity one would choose a monofunctional styrene-DVB resin of tertiary or quaternary amine functionality.

The chloride preferences exhibited by these resins also appear to be much influenced by the matrix type and to a lesser extent by the functionality. Again styrene-DVB resins, especially tertiary amines, are the preferred types for nitrate removal in the presence of the competing ions — chloride and sulfate.

We had yet to examine the effects of such variables as capacity, porosity and pKa on the sulfate and chloride preferences of the resins. Since these in addition to matrix and functionality are all controllable variables one would ideally like to quantify their contributions to the dependent variables α_N^S and α_{Cl}^N so as to be able to predict these selectivities for

available resins and to control them when making new resins. This objective resulted in a need to perform a comprehensive statistical analysis on the data gathered from laboratory experiments and from the resin manufacturers. That analysis is the subject of the next section.

STATISTICAL ANALYSIS OF RESIN DATA

Objective

The overall objective of the statistical analysis of the Phase I data was to develop a predictive equation or equations relating to the dependent variables α_N^S and α_{Cl}^N to a minimum number of relevant independent variables from the list:

- matrix type
- functionality
- ion-exchange capacity
- porosity
- pKa
- quaternary type (I or II)

Of the seven variables, four are represented by interval data (measured on a ratio scale) and the remaining three, matrix, functionality and porosity are categorical in nature. Straight-forward statistical analysis e.g. multiple linear regression was not possible because of the combination of categorical and interval scale variables.

Data Summaries

Twenty-nine of the 32 resins evaluated are listed in Table 3 where they are characterized by particular values of the seven variables just discussed. Three of the resins tested were eliminated from the data analysis because they represented single-case categories of strong-base styrene-DVB resins which were already over represented. Styrene-DVB resins comprise 16 of the 29 resins (cases) evaluated statistically.

TABLE 3: ANION RESIN CHARACTERISTICS

UM Resin Number	Manufacturer's Designation	Matrix	Functionality	Porosity	meq/ml Advertised Capacity	meq/ml Measured HCl Capacity	pKa	Average α_N	Average α_{Cl}
15	AMBERLITE IRA-400	STY-DVB	Q-1	MICRO	1.40	1.53	>13	1.89	-
17	AMBERLITE IRA-900	STY-DVB	Q-1	MACRO	1.00	1.10	>13	1.71	3.41
21	DOWEX SBR	STY-DVB	Q-1	MICRO	1.40	1.66	>13	1.89	2.90
27	IONAC ASB-1	STY-DVB	Q-1	MICRO	1.40	1.39	>13	1.87	-
32	IONAC AFP-100	STY-DVB	Q-1	MACRO	1.20	1.07	>13	1.76	2.97
16	AMBERLITE IRA-400	STY-DVB	Q-1	ISO	1.25	1.16	>13	3.09	3.11
19	DOWEX SBR-P	STY-DVB	Q-1	ISO	1.20	1.02	>13	2.96	-
22	DOWEX 11	STY-DVB	Q-1	ISO	1.20	1.17	>13	3.37	-
24	DUOLITE A-101-D	STY-DVB	Q-1	ISO	1.30	1.32	>13	2.59	-
28	IONAC A-641	STY-DVB	Q-1	FM	1.16	1.21	>13	3.30	3.30
30	IONAC ASB-1P	STY-DVB	Q-1	ISO	1.35	1.13	>13	2.59	-
14	AMBERLITE IRA-910	STY-DVB	Q-2	MACRO	1.00	1.31	>13	3.26	2.85
18	AMBERLITE IRA-410	STY-DVB	Q-2	MICRO	1.35	-	>13	2.40	-
20	DOWEX SAR	STY-DVB	Q-2	MICRO	1.40	1.50	>13	3.04	-
23	DUOLITE A-102-D	STY-DVB	Q-2	MICRO	1.40	1.48	>13	3.26	-
29	IONAC ASB-2	STY-DVB	Q-2	MICRO	1.52	1.33	>13	3.04	3.64
1	AMBERLITE IRA-93	STY-DVB	TERTIARY	MACRO	1.25	0.98	7.7	3.75	4.86
5	DOWEX MWA-1	STY-DVB	TERTIARY	MACRO	1.10	1.15	7.6	2.67	4.43
8	DUOLITE ES-368	STY-DVB	TERTIARY	MACRO	1.30	1.43	7.8	2.83	3.87
12	IONAC AFP-329	STY-DVB	TERTIARY	MACRO	1.25	1.26	8.5	3.07	4.14
3	AMBERLITE IR-45	STY-DVB	POLY	MICRO	1.90	1.76	7.9	12.7	3.89
2	AMBERLITE IRA-68	ACRYLIC-AMINE	TERTIARY	MICRO	1.60	1.42	11.1	23.4	1.89
10	DUOLITE ES-374	ACRYLIC-AMINE	POLY*	MACRO	3.0	2.59	9.9	94.0	3.85
6	DUOLITE A-7	PHENOL-HCHO-PA	POLY**	MACRO	2.4	1.67	7.7	108	3.35
9	DUOLITE ES-561	PHENOL-HCHO-PA	POLY	MACRO	2.0	1.22	6.8	109	2.65
11	IONAC A-260	ALIPHATIC-AMINE	POLY	MICRO	1.8	1.81	10.6	54.0	2.25
4	DOWEX WGR	EPOXY-AMINE	POLY	MICRO	1.0	1.53	7.9	137	1.99
7	DUOLITE A-340	EPOXY-AMINE	POLY	MICRO	2.6	2.54	8.7	82.9	1.70
13	IONAC A-305	EPOXY-AMINE	POLY+	MICRO	3.5	1.51	108	108	-

POLY = Polyamine not including quaternary amine
 Q-1 = Quaternary Amine - Type 1
 Q-2 = Quaternary Amine - Type 2
 ISO = Isoporosity or "Improved Porosity"
 FM = Fixed Macropore (MANUFACTURER'S TERMINOLOGY)
 POLY* = Advertised as tertiary amine but titrates as polyamine
 POLY** = Advertised as secondary amine but titrates as polyamine
 POLY+ = Polyamine including quaternary amine

Table F1 (Appendix) is a listing of the computer datafile derived from the resin data in Table 3. Missing data is coded - 0.0. Representative data are coded as follows:

Variable 1, V1, (dependent, interval scale, dimensionless)

Average sulfate/nitrate separation factor: α_{N}^S

Range: 1.71 to 137

Variable 2, V2, (dependent, interval scale, dimensionless)

Average nitrate/chloride separation factor: α_{Cl}^N

Range: 1.7 to 4.86

Variable 3, V3, (independent, interval scale, meq/ml)

Measured HCl capacity

Range: 0.98 to 2.59

Variable 4, V4, (independent, interval scale, dimensionless)

pKa for HCl

Range: 6.8 to 13

All strong base resins were assumed to have pKa = 13

Variable 5, V5, (independent, categorical)

Functionality

polyamine = 2; (8 cases)

tertiary amine = 3; (5 cases)

quaternary amine = 4; (16 cases)

Variable 6, V6 (independent, categorical)

Matrix Type

styrene - DVB = 1; (21 cases)

acrylic amine = 2; (2 cases)

phenol - HCHO = 5; (3 cases)

aliphatic amine = 6; (1 case)

Variable 7, V7 (independent, categorical)

Porosity

 Microporous or Gel = 1, (13 cases)

 Macroporous or macroreticular = 2, (10 cases)

 Isoporous or "improved porosity" = 3, (6 cases)

Variable 8, V8 (independent, categorical)

Nitrogen in polymer backbone or out-of-backbone

 nitrogen in = 1, (8 cases)

 nitrogen out = 2, (21 cases)

Variable 9, V9 (dependent, interval-scale, dimensionless)

Log_e of α_N^S

Range = 0.57 to 4.92

Variable 10, V10 (dependent, interval-scale dimensionless)

Log_e of α_{Cl}^N

Range = 0.53 to 1.58

Dummy Variable 11, V11, (independent, interval-scale, dimensionless)

Relative crystal ionic radius of functional group

 Secondary amine = 2.00

 Tertiary amine = 2.19

 Quaternary amine = 2.36

Dummy Variable 12, V12, (independent, interval-scale, dimensionless)

Nitrogen position in resin

(related to distance of separation of charged sites)

 nitrogen out of polymer backbone = 0.00 (far away)

 nitrogen in polymer backbone = 1.00 (close)

Variable 13, V13 (dependent, categorical)

Quaternary functional group type

 Type 1 = 1 (11 cases)

 Type 2 = 2 (5 cases)

Variable 14, V14 (independent, interval-scale, dimensionless)

Relative degree of crosslinking

Isoporous resins = 0.5

Microporous resins = 1.0

Macroporous resins = 2.0

MIDAS: Michigan Interactive Data Analysis System

Actual computations of the statistics were accomplished using the extensive UM computing facilities (Michigan Terminal System) with the aid of the MIDAS system of data analyses and statistical computing programs developed by the UM Statistical Research Lab. Documentation for the MIDAS system is presented in Reference [48] while interpretation of statistical techniques are given in Reference [124].

The particularly desirable features of the system are its ability to handle both categorical and analytical (interval-scale) variables, its intuitive syntax, its capability for partitioning the dataset, and its excellent documentation.

The Dependent Variables of Interest: $\alpha_N^S, \alpha_{Cl}^N$

Separation Factor vs Selectivity Coefficient

In an earlier discussion it was pointed out that the separation factor, α_j^i , differs from the selectivity coefficient K_j^i when ions of dissimilar valence are exchanged. Although the selectivity coefficient is theoretically more satisfying, its magnitude gives no simple indication of the preference which a given resin has for the ions of interest at an established total concentration e.g. 0.005N (250 ppm CaCO_3). The binary separation factor, on the other hand, being simply the ratio of the distributions of ions between phases given a clear intuition of the preference which the resin has between the ions of interest.

For all the resins tested, the α_N^S 's are greater than 1.0 indicating a clear preference for SO_4 ions over NO_3^- ions. Similarly, all the resins exhibited α_N^{Cl} 's of less than 1.0 indicating a preference of NO_3^- over Cl^- . Additional arguments for the choice of separation factors over selectivity coefficients are presented in Appendix E: Calculation E3.

The Calculation of Average Separation Factor

It may be observed graphically, that all of the resins having low sulfate selectivity (tertiary and quaternary styrene-DVB resins) also have modest inflection points in their isotherms. Hence, the simplest mathematical model (without theoretical basis) which could be used to describe the curve would involve a cubic equation, again giving rise to much more complexity and to parameters like the selectivity coefficient which give no intuitive indication of the actual preference the resin has for one ion over another. Having chosen to use the separation factor to describe each isotherm the task remaining was to arrive at a satisfactory means of determining the best, single factor describing the curve. Using a simple averaging technique where the mean separation factor determined at three or more points on an isotherm at say $X = 0.25, 0.50$, and 0.75 , was rejected on the basis that it utilized a minimum amount of the data available and that the selection of points would be arbitrary.

Linear Regression Technique for Average α_j^i

A least-squares regression technique was attempted on several representative isotherms including the styrene-DVB resins numbered 3 and 8. (Figures A33 and A34) The constant separation factor description of an isotherm may be linearized for the statistical regression analysis as follows:

$$\alpha_j^i = \frac{y_i x_j}{x_i y_j} \quad (14)$$

$$x_j = 1 - x_i$$

$$y_j = 1 - y_i$$

$$\frac{y_i}{1-y_i} = \alpha_j^i \frac{x_i}{1-x_i} \quad (20)$$

Using the five or six experimentally determined points (y_{i1} , x_{j1} ; y_{i2} , x_{j2} ; etc) plots of $\frac{y}{1-y}$ vs. $\frac{x}{1-x}$ were made for several of the isotherms. The calculated, least squares, linear regression line was drawn through the data, and the α_j^i determined from its slope. This statistically determined α_j^i was then used to construct the "Regression" isotherm on the usual coordinates to determine how it fit the original data points. The fit was not at all good for the sulfate/nitrate isotherms and only a fair approximation for the chloride/nitrate isotherms (see Figures A33 and A34). The reason for the poor fit is obvious. During the linearization procedure, some extreme values were created which almost entirely determined the slope of the regression line. The least squares, linear regression technique produces a "best fit" of the linearized $\frac{y}{1-y}$ vs $\frac{x}{1-x}$ equation but certainly not for the original y vs x relationship. Note that the "Regression" isotherms in Figures A33 and A34 are nearly perfect fits of the data in the range of $X = 0.8$ to $X = 1.0$ which is just what one would expect since points in this range are responsible for the extreme values created in the linearization process.

The Ratio of Areas Technique for Average α_j^i

The example isotherm (Figure 4) illustrates that the separation factor can be represented as the ratio of rectangular area 1, [equal to $y(1-x)$] below the isotherm, to rectangular

area II [equal to $x(1-y)$] above the isotherm. Mathematically it can be shown (see Appendix E) that the separation factor is related to the ratio of the entire area below the isotherm to the entire area above it by the following relationship.

$$R_a = \frac{\text{entire area under isotherm}}{\text{entire area above isotherm}} \quad (21)$$

$$R_a = \frac{\frac{(\alpha^2 - \alpha - \alpha \ln \alpha)}{(\alpha - 1)^2}}{1 - \frac{(\alpha^2 - \alpha - \alpha \ln \alpha)}{(\alpha - 1)^2}} \quad (22)$$

To estimate the best fit separation factor by the ratio of areas technique developed here, the areas were measured by planimeter, the ratio R_a determined and α calculated by trial and error solution of equation 22. The calculated α 's, referred to as the average separation factors were then used to construct the best fit, constant separation factor isotherms as shown in Figures A35 and A36. Clearly, the ratio of areas technique produces a much better fit of the original data than does the linearized, least-squares method. Thus, average separation factors so calculated were used to represent the sulfate/nitrate and nitrate/chloride selectivities of the 29 resin analyzed statistically. Note that in Figures A33 and A34, the chloride/nitrate experimental data is very well represented by a constant separation factor isotherm which is as expected for univalent-univalent ion exchange. The sulfate/nitrate isotherm with an inflection, Figure A34, is only modestly well fitted by a constant α while isotherms without inflections of the type shown in Figure A33 are well represented by a constant α .

Resin Characterization by Independent Variables

Resin Capacity--

This is the total wet-volume exchange capacity determined for HCl in 2N solution. The capacity determination procedure is given in Appendix D. For all the strong-base resins, measured capacities were in rather good agreement with the advertised values. Such was not the case with all the weak-base resins especially those with polyamine functionality. One resin (No. 4), Dowex WGR had a significantly higher capacity than advertised and four others (No.'s 6, 9, 10 and 13), Duolites A-7, ES-361 and ES-374 and Ionac A-305 had significantly lower capacities than advertised. With these weak-base resins, capacity was, as expected, a function of the type of acid and the pH of equilibration as evidenced by the titration curves (Figs. B1-B12) where it is seen that H_2SO_4 yields the highest capacities, HCl the lowest with HNO_3 being intermediate between the two. This also is generally the order of preference of the anions of those acids by the resins.

Resin pKa's--

Weak base resin pKa's were determined for HCl, HNO_3 and H_2SO_4 by the titration technique described in the Appendix: procedure D5. These numbers are not particularly reliable because of obvious difficulties encountered in determination of the end points of the inflectionless titration curves shown in Figures 84, 86, 87, 89, B10 and B11. In these instances the measured, total, wet-volume, HCl capacity was used as the endpoint. These pKa's should be considered as relative values only because of the nature of the assumptions used in the derivations. [Ref. 60, p. 84].

Strong-base resins pKa's were not determined experimentally as they were all expected to be nearly equal at a value > 13 [Ref. 60, p. 86]. For the sole purposes of statistical analysis

the estimated value of $pK_a = 13$ was assigned to all strong-base anion resins.

Amine Functionality--

A given resin was either primary, secondary, tertiary, quarternary or a combination of these labelled polyamine which as it turned out comprised mainly secondary amines with lesser amounts of the primary and tertiary varieties.

Evaluations of the titration curves (Figs. B1-B12) in combination with the manufacturers stated description of functionality resulted in the observation that the only monofunctional weak-base resins (having essentially a single type of functional group) were those advertised to be tertiary amines (resins 1, 2, 5, 8 & 12) with the exception of Duolite ES-374, advertised to be tertiary but which titrated as a polyamine type. Consequently, all the remaining weak-base resins were labelled as polyamines and characterized as being basically secondary amines with some primary and tertiary groups present. (Resins 3, 4, 6, 7, 9, 10 and 11).

Matrix Type--

This is a description of the organic polymer backbone of the resin. According to written and verbal information supplied by the manufacturers (data sheet and personal communications), five distinct polymers were represented in this study: polystyrene crosslinked with divinylbenzene (STY-DVB), polyacrylic-acid polyamine condensation polymers (acrylic-amine), phenol-formaldehyde-polyamine condensation polymers (phenol-HCHO-PA), epichlorohydrin-polyamine condensation polymers (epoxy-amine), and an acetone-formaldehyde polyamine condensation polymer (aliphatic-amine).

It should be noted that with the exception of the STY-DVB resins, the nitrogen-bearing functional groups are incorporated (polymerized) into the backbone where they are probably separated

there by no more than the distance of separation of the nitrogen atoms in the amine monomers used in polymerization. The importance of this proximity of positively charged nitrogen atoms is shown later when it is hypothesized as being the primary cause of sulfate selectivity as N in the matrix always gives the rise to high values of α_N^S .

Degree of Cross Linking--

Cross linking is the achievement of a three dimensional polymer network by the cross as opposed to linear bridging of polymer chains through chemical bonding. With polystyrene based, cation resins this cross linking is easily quantified as the % of divinylbenzene (DVB) in the matrix. High degrees of cross linking (e.g. 12% DVB) produce tight structures favoring smaller ions, are hard, mechanically and chemically stable and kinetically slow. The opposite is true for low degrees of cross linking (e.g. 4% DVB). Characterization of anion resins by degree of cross linking is most difficult whether they contain DVB or not (Dorfner p. 33, R. Anderson Personal Communication).

Styrene-DVB anion resins are capable of methylene bridging between benzene rings as a result of chloromethylation prior to the required amination step. So the % DVB doesn't truly characterize the degree of crosslinking for these resins. The non-styrene based resins don't even contain DVB. Their cross linking takes place through the nitrogen in the matrix. Since this is a study of anion resins for which the degree of cross linking has not been well characterized, this possible variable could not be readily included in the statistical analysis. However, a category akin to the degree of cross linking is the resin porosity for which data do exist, so it was included for analysis.

Porosity--

Unfortunately resin manufacturers use a variety of labels to categorize resins as to porosity - a measure of the degree of openness of the polymer matrix related to the type and degree of crosslinking.

In this report, the distinction between gel and macroreticular resins used elsewhere is adhered to [Ref. 40, p. 37; Ref. 60, p. 60]. Gel resins are microporous having an apparent porosity of atomic dimensions (10-20Å) whereas macroreticular or macroporous resins, whose beads comprise aggregates of gel resins, have internal voids with dimensions far exceeding atomic distances of separation (up to several hundred angstroms). Still a third type of porosity is available among the styrene-DVB strong-base resins, i.e., isoporous resins. These are also loosely referred to as polystyrene resins with a "higher degree of porosity" than gel resins (Ionac and Amberlite data sheets) or as having "porous structure" (Duolite and Dow Data Sheets) or simply as being "porose" (Boari p. 153). There are then three types of porosity represented here: microporous, macroporous and isoporous. For polystyrene-based resins the degree of cross linking is related to these classifications as follows:

Gel: Polymerization step with 6-8% DVB then chloromethylation - little secondary crosslinking due to methylene bridging.

Product is generally transparent.

Macroporous: Polymerization with high degree of DVB cross linking before chloromethylation and aggregate bead formation. Product is opaque.

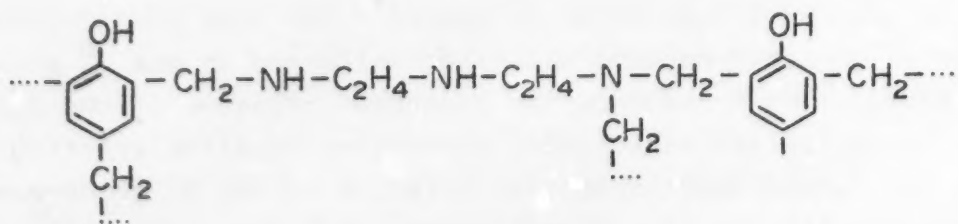
Isoporous: Polymerization step with very low degree (0.5 to 2.0%) of DVB crosslinking followed by chloromethylation and significant degree of methylene bridging. Product is transparent and more porous than gel with lower degree of effective crosslinking.

Note: During the statistical analysis of the data an interval scale variable (XLINKING, V 14) relating porosity to the estimated relative degree of crosslinking was created in an attempt to improve the prediction of nitrate/chloride selectivity.

Nitrogen Position: Nitrogen N2POSITN--

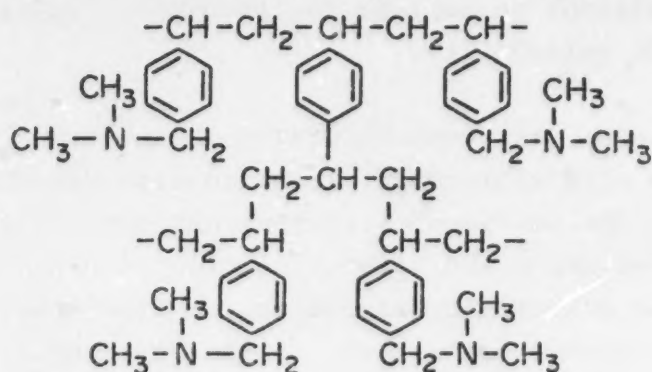
This is a straightforward classification based on the observation that the matrices: epoxy-amine, acrylic-amine, phenol-formaldehyde-polyamine and aliphatic-amine invariably gave rise to high sulfate selectivity regardless of functionality. The common characteristic among these is the presence of the amines during the polymerization step giving rise to nitrogen linking and crosslinking in the polymer making it an inherent part of the continuous structure. This is contrasted to the case with polystyrene-based resins where amination takes place after polymerization and chloromethylation yielding a matrix containing the active nitrogen atom strictly as a part of a pendant, amine molecule connected through a methylene group to the continuous cross-linked polymer matrix.

Nitrogen in the matrix e.g. in a phenol-formaldehyde-polyamine resin is symbolically represented as:



Nitrogen in the Matrix

whereas pendant nitrogen, out of the polystyrene matrix is represented as:



Nitrogen out of the Matrix (Pendant)

For reasons to be discussed later, these differences appeared to greatly affect sulfate selectivity.

Size of Functional Group: RSIZE--

It has been reported that the nature of the functional group especially its size and charge density have a significant effect on anion selectivity [60, 21, 40, 39, 75, 78, 99, 113 and 129]. Boari, Liberti et. al. [13] have recently given special attention to the effect of the functional group on the sulfate/chloride selectivity of strong and weak-base anion exchangers for use in removing sulfate from sea water prior to multi-stage, flash evaporation. In their work $\alpha_{\text{Cl}}^{\text{S}}$ was found to increase as the size of the functional group decreased. The same physicochemical effect is expected to have a similar influence on the $\alpha_{\text{N}}^{\text{S}}$ separation factor. To accommodate the expected influence of the functional group in the anticipated predictive equation relating $\alpha_{\text{N}}^{\text{S}}$ to the independent variables, relative values of group size were assigned to the functional groups as follows:

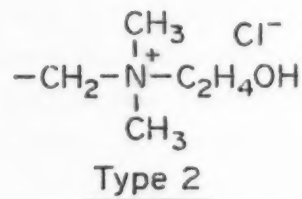
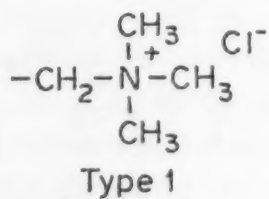
TABLE 4 [13]: SIZES OF FUNCTIONAL GROUPS

Functionality	Crystal Ionic Radius A°	Relative Ionic Radius
primary	-	-
secondary	2.97	2.00
tertiary	3.27	2.19
quaternary	3.49	2.36

Should the influence of size predominantly control the relationship between α_N^S and functionality, the newly created, interval-scale variable, relative ionic size (RSIZE) should be statistically correlated (negatively) to the sulfate/nitrate selectivity ($\ln \alpha_N^S$). Note that there is no need to assign a relative size to primary amines as they are grouped with polyamines which are scored as secondary amines where applicable.

Quaternary-Amine Type: TYPE

It was not anticipated that the type of functional group would have a significant influence on either α_N^S or α_{Cl}^N . However, examination of the respective isotherms resulted in the tentative conclusion that the quaternary type does measurable affect α_N^S but not α_{Cl}^N . Recall that the different types are:



and that type 1 being a stronger base is harder to regenerate (with alkali). For groundwater deionization the choice between

types 1 and 2 would be made on the basis of ionic preferences and ease of regeneration not on the advertised fact that type 1 is more resistant to oxidation or that type 2 offers greater thermal resistance - these latter considerations not being relevant.

Results of the Statistical Analysis

Overview--

A rather lengthy and complicated statistical analysis provided a hopefully unbiased look at the significant, insignificant and questionable relationships among the variables. Quantification of these relationships followed by an assessment of level of significance was then accomplished. Given that a test statistic had been calculated, e.g. the "F" statistic, the level of significance which was assigned to it was very much a function of the sample size with small samples obviously requiring large values of the test statistics to be considered significant at the usually accepted levels of 0.05 to 0.01. The strength of this particular set of data appears to lie in the sensitivity of the dependent variables especially α_N^S (and $\ln \alpha_N^S$) to changes in the independent variables. Its weakness lies in the small sizes of some of the samples used in the various tests. It will be shown however that after having both of these factors into consideration, some very significant relationships were developed.

Recall that the objective of statistical analysis was to develop predictive equations relating α_N^S and α_{Cl}^N to capacity, matrix, functionality, pKa, porosity and quaternary type.

Statistical Correlations

The Correlation Matrix: All Resins Considered--

Table F4 (Appendix) is the correlation matrix for all the interval scale variables (1, 2, 3, 4, 9, 10, 11, 12) with all resins (cases 1-32) considered. The matrix is a tabulation of the Pearson, product-moment correlation coefficients (r) each of which described the strength of the linear relationship between a pair of variables. Pearson's " r " is dimensionless, and ranges from -1.0 to +1.0 with these limits denoting perfect, linear, negative or positive relationships respectively. The square of the correlation coefficient (r^2) known as the "coefficient of determination" can be interpreted as being that fraction of the total variability in one of the variables which can be explained by the least squares regression line relating it to the second variable. For this particular matrix only 19 of the 32 resins (12 weak base and 7 strong base) were considered i.e. only those having complete data for all the variables considered. For a relationship to be considered significant at the .05 and .01 levels, correlation coefficients of $\pm .4555$ and $\pm .5751$ respectively are required. Table 6 below summarizes the non-trivial correlations listed in Table F4. Both α_j^i and $\ln \alpha_j^i$ were included in Table 6 to show (1) that $\ln \alpha_j^i$ produces higher correlations and that (2) the use of either $\ln \alpha_j^i$ or α_j^i leads to essentially the same conclusions which are that sulfate/nitrate selectivity is influenced by:

Matrix > Functionality > Capacity

and that chloride/nitrate selectivity is influenced by:

Matrix and Crosslinking >> All other variables

Maximum nitrate selectivity then is favored by:

- (1) Nitrogen out of the matrix (Polystyrene resins with a relatively greater distance between charged sites)
- (2) Quaternary and tertiary amine functionality
- (3) Low capacity

Finally, examination of the last two entries in Table 6 reveals

that chloride selectivity is unrelated to functionality. Clearly then matrix is the most important determinant of overall nitrate selectivity with respect to sulfate, chloride and bi-carbonate.

The Correlation Matrix: Weak Base Resins--

Table F2 (Appendix) is the correlation coefficient matrix for the weak-base resins (cases 1-13) considered as a group separate from strong-base resins. The non-trivial correlations contained in that matrix are summarized in Table 5 below. Compared to the correlations among all resins (Table F4), fewer cases are represented here, consequently correlation coefficients of ± 0.5760 and ± 0.7079 are required for significance. At the .05 and .01 levels respectively.

TABLE 5. MEANINGFUL CORRELATIONS:
WEAK BASE RESINS ONLY

Variables Considered	r Correlation Coefficient	100 r ² % Variation Explained
$\ln \alpha_N^S$ with N Position	.93*	86
$\ln \alpha_N^S$ with "R" Group Size	-.87*	76
$\ln \alpha_{Cl}^N$ with N Position	-.78*	61
$\ln \alpha_{Cl}^N$ with Relative Crosslinking	.75*	56
$\ln \alpha_N^S$ with $\ln \alpha_{Cl}^N$	-.67	45
"R" Group Size with N Position	-.66	44
Capacity with "R" Group Size	-.63	40
$\ln \alpha_N^S$ with Capacity	.57	32

* = Significant at the .01 level

TABLE 6

MEANINGFUL CORRELATIONS: WEAK AND STRONG-BASE RESINS

Variables Considered	r Correlation Coefficient	100 r ² % Variation Explained
$\ln \alpha_N^S$ with N Position	.95*	90
α_N^S with N Position	.88*	77
$\ln \alpha_N^S$ with "R" Group Size	-.88*	77
α_N^S with "R" Group Size	-.79*	62
"R" Group Size with N Position	.77*	59
$\ln \alpha_{Cl}^N$ with N Position	-.65*	42
α_{Cl}^N with N Position	-.62*	38
$\ln \alpha_N^S$ with Capacity	.63*	40
α_N^S with Capacity	.53*	28
Capacity with "R" Group Size	-.61*	37
Capacity with N Position	.60*	36
$\ln \alpha_N^S$ with $\ln \alpha_{Cl}^N$	-.53	28
α_N^S with α_{Cl}^N	-.46	21
$\ln \alpha_N^S$ with pK_a	-.53	28
α_N^S with pK_a	-.53	28
$\ln \alpha_{Cl}^N$ with "R" Group Size	.25	6
α_{Cl}^N with "R" Group Size	.20	4

* = Significant at the .01 level

The Correlation Matrix: Strong Base Resins

Considering only the strong base resins as a group led to the elimination of three possible dependent variables from consideration: pK_a , NPOSITIN and RSIZE. All have the same pK_a (13), all are quaternary (RSIZE= Const.) and all are polystyrene (N out of matrix). The remaining possible correlations are among $\ln \alpha_N^S$, $\ln \alpha_{Cl}^N$ and capacity. There are no significant correlations among these as is seen by examination of table F3 (Appendix).

The nitrate selectivity of strong base resins is not predictable from the interval scale data available. Nevertheless, some control over this selectivity can be achieved as a result of controlling the type and porosity variables: a fact which can be demonstrated by the analysis of variance technique.

Analysis of Variance: ANOVA

The ANOVA Method

Among the categorized variables which hadn't initially been converted to interval-scale, dummy variables were porosity (V5) and quaternary type (V13). These did appear to affect the sulfate selectivity during visual inspection of the original isotherms so, Type I, gel and macroporous resins were plotted together in a composite isotherm (Figure 15), as were the Type I, isoporous resins (Figure 16), and Type II, gel and macroporous resins (Figure 17). One way analysis of variance was performed on the data to quantify these effects and to verify the correlations between the selectivities ($\ln \alpha_N^S$, $\ln \alpha_{Cl}^N$) and the categorized variables (matrix and functionality) which had been converted to interval-scale variables (NPOSITIN and RSIZE).

The ANOVA technique makes use of the F statistic to compare the group sample means of a dependent variable, select cases of which have been assigned to these groups which are sub-

divisions of some independent, categorical variable. Consider, for example, the effect of matrix on sulfate/nitrate selectivity ($\ln \alpha_N^S$) where there were five categories, each corresponding to one of the five matrices. The program computed the mean $\ln \alpha_N^S$ of each category and a grand mean considering all the values of $\ln \alpha_N^S$. The variance represented by the mean sum of squared deviations within each category was then compared to the variance between categories by taking the ratio:

$$F = \frac{\text{Mean sum of squares between categories}}{\text{Mean sum of square within categories}} \quad (23)$$

For this particular example, the higher the F ratio, the more significant was the effect of matrix on selectivity as compared to that expected from random statistical variations.

The null hypothesis here (H_0) was that the mean $\ln \alpha_N^S$ was the same for all categories. For $F \gg 1.0$ we tended to reject the null hypothesis, and the corresponding level of significance (SIGNIF) attained (a function of the number of cases and the number of categories) was the probability of being wrong when making the decision. The "% variation among" statistic is the variance explainable due to the categorization — matrix in the example.

Tables 9 and 10, following, summarize the effects of the important categorical variables on sulfate/nitrate and nitrate/chloride selectivity. An unexpected result contained therein is that porosity somehow influences the nitrate/chloride preferences of weak-base anion resins (WBA).

Effect of Matrix and Functionality on Selectivity: ANOVA Technique

The sulfate/nitrate selectivity of all resins as a group, and of weak-base anions resins as a group, clearly relates to both matrix and functionality (Table 9, A-H) as indicated by the

extreme values of the F statistic ($F \gg 1.0$). Generally, the F statistic is not as high for WBA resins compared to all resins (e.g., compare A&B, C&D, E&F). This appears to be due to the reduction in the range of $\ln \alpha_N^S$ values or to the fewer functional groups considered when looking at only WBA resins compared to all resins. That the matrix categorization based on nitrogen-in-or-out of the matrix is useful is borne out by comparison of F statistics (A&C, B&D) where the nitrogen in-or-out classification yields higher, more significant results than does the five-matrix categorization. It will be shown later in the discussion of the regression equations that this dichotomized, matrix variable provided a simple and direct means for the matrix effect to be included in the prediction equations for selectivity.

Nitrate/chloride selectivity (Table 10; a-d) is influenced by matrix more than by any other single variable including functionality (Table 9; e,f) which is nearly inconsequential in explaining variations in $\ln \alpha_{Cl}^N$. Obviously this means that matrix is the single, most-important variable for predicting overall nitrate selectivity with respect to both sulfate and chloride — the problem at hand.

The combination, matrix * functionality, produces categories corresponding to all combinations of these variables, e.g.: STY-DVB-tertiary amine, STY-DVB-polyamine, etc. Sulfate/nitrate selectivity would appear to be almost completely explained by these combinations (Table 9; G,H) with 98.9% and 98.5% variation among categories for all resins and for WBA resins respectively. For nitrate/chloride selectivity, such is not quite the case; the combination, matrix * functionality, is an improvement over matrix alone but not nearly so much as in the former case.

These ANOVA findings based on the original categorical

variables are completely supportive of those derived from dummy variable analysis by correlation, regression and selection of regression. For that reason they have been included; also, they make obvious some previously obscure relationships between porosity and nitrate/chloride selectivity.

Effect of Porosity on Selectivity: ANOVA Technique

Categorizing all resins according to porosity and comparing mean $\ln \alpha_N^S$'s indicated no real differences due to porosity (Table 9; I). However, from insight gained during visual inspection of the isotherms, the sulfate/nitrate selectivity of Type I, strong-base anion (SBA) resins did appear to be a function of whether a given resin was isoporous or not-isoporous (i.e., gel or macroreticular). ANOVA L, Table 9 corroborated this apparent relationship with an F statistic of 76.5. Type I, isoporous SBA resins have measurably higher sulfate selectivity (average $\alpha_N^S = 2.97$) than do Type I gel or macroporous resins (average $\alpha_N^S = 1.82$). This sort of porosity effect was not noted however with nitrate/chloride selectivity and Type I, isoporous SBA resins. In fact, porosity seemed to have no effect at all on the $\ln \alpha_{Cl}^N$ of SBA resins in general as documented in Table 9; entries K & L.

Although it was not discernible during inspection of the chloride/nitrate isotherms (Figures A1-A32), porosity accounted for 37.8% of the variance in $\ln \alpha_{Cl}^N$ among all resins and 66.5% of the variance in $\ln \alpha_{Cl}^N$ for WBA resins (See Table 10; i & j). Overall, the relationship appears to be significant only for WBA resins since we have just seen that porosity doesn't account for any variability among the SBA resins. At first it was thought that this was a secondary effect - porosity being somehow highly correlated with another relevant variable like matrix. To check this, porosity was converted to a dummy variable (XLINKING) which is the estimated, relative degree of cross linking.

TABLE 7. POROSITY RELATED TO RELATIVE DEGREE OF CROSSLINKING

Porosity	Estimated % Crosslinking	Relative Degree of Crosslinking
Isoporous	3	.5
Microporous	6	1.0
Macroporous	12	2.0

In the WBA resin correlation matrix (Appendix: Table F2) XLINKING is only modestly correlated ($r = .27$) with the important variables: nitrogen position (N2POSITN), and "R" group size (RSIZE) with r 's of 0.37 to -0.37 respectively.

This lack of significant correlation between XLINKING and the other dependent variables was an encouraging sign that it's presence would add reliability to the predictive equation for nitrate/chloride selectivity. Also, the case for porosity being a determinant of nitrate/chloride selectivity among WBA resins was strengthened but difficult to explain. Close scrutiny of the average α_{Cl}^N data in Table 10 indicates that the porosity-selectivity relationship exists only for resins with nitrogen in the matrix; no such relationship exists among the polystyrene resins.

Effect of Quaternary Type: ANOVA Technique

As indicated by the sulfate/nitrate isotherm in Figures 15 and 17, the quaternary type does significantly influence sulfate selectivity; this is verified by ANOVA M, Table 9 (F=67). Table 8 below summarizes these effects for strong base resins.

TABLE 8. EFFECTS OF POROSITY AND TYPE
ON SULFATE/NITRATE SELECTIVITY

Resin	Average α_N^S
Type I, SBA, Gel and MR	1.82
Type II, SBA, Gel and MR	2.98
Type I, SBA, Isoporous	2.97

Quaternary type doesn't influence nitrate/chloride selectivity at all as verified by ANOVA M, Table 9 ($F = 0.147$).

Regression Equations and Scatter Plots

Simple, Linear Regression Analysis and Plotting--

Here an attempt has been made to predict the value of either $\ln \alpha_N^S$ or $\ln \alpha_{Cl}^N$ knowing the value of one of the following interval-scale variables: CAPACITY, pKa, RSIZE or N2POSITN. This was accomplished using the linear least-squares regression technique the results of which were plotted on the scatter plots to give a feel for the degree to which the line actually fit or didn't fit the data since correlation coefficients (r 's) can be very misleading. Usually, high correlation coefficients (e.g., .90 or .95) suggest mental pictures of better curve fits than actually exist.

Effect of Capacity and Nitrogen Position on α_N^S and α_{Cl}^N --

Capacity is expected to influence the preference of an ion exchanger for multivalent ions (e.g. $SO_4^{=}$) as compared to monovalent ions (e.g. NO_3^-): "As a rule the ion-exchanger prefers the counter ion of higher valence The preference increases with dilution of the solution and is strongest with ion exchangers of high internal molality" [60]. Ames [4, 5] attempted

TABLE 9

ANALYSIS OF VARIANCE:

VARIABLES EXPLAINING SULFATE/NITRATE SELECTIVITY: $\ln \frac{S}{N}$

ANOVA DESIG.	CASES CONSIDERED	STRATIFICATION (CATEGORIES EXAMINED)	F STAT.	LEVEL OF SIGNIF.	VARIATION AMONG CATEGORIES
A	All Resins	Matrix (STY-DVB), (Acrylic), (Phenolic) (Epoxy), (Aliphatic)	86.2	.0000	96.3
B	WBA Resins	Matrix (STY-DVB), (Acrylic), (Phenolic) (Epoxy), (Aliphatic)	20.5	.0003	89.0
C	All Resins	Matrix (Nitrogen in), (Nitrogen out)	304	.0000	96.3
D	WBA Resins	Matrix (Nitrogen in), (Nitrogen out)	76.3	.0000	92.4
E	All Resins	Functionality (Poly), (Tertiary), (Quat.)	95.2	.0000	91.7
F	WBA Resins	Functionality (Poly), (Tertiary)	35.1	.0001	84.7
G	All Resins	Matrix * Functionality (All Combinations of Matrix and Functionality)	179	.0000	98.5
H	WBA Resins	Matrix * Functionality (All Combinations of Matrix and Functionality)	162	.0000	98.9
I	All Resins	Porosity (Micro), (Macro), (Iso)	1.24	.3036	2.6
L	Type I SBA Resins	Porosity (Gel or MR), (Iso)	76.5	.0000	93.3
M	Gel & MR SBA Resins	Type (I, Gel or MR), (II, Gel or MR)	67.0	.0000	93.0

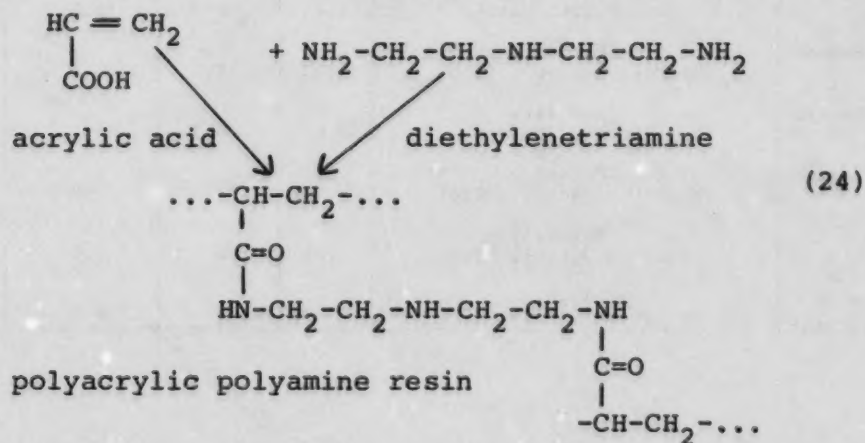
TABLE 10

ANALYSIS OF VARIANCE:

VARIABLES EXPLAINING NITRATE/CHLORIDE SELECTIVITY: $\ln \alpha_{Cl}^N$

ANOVA DESIG.	CASES CONSIDERED	STRATIFICATION (CATEGORIES EXAMINED)	F STAT.	LEVEL OF SIGNIF.	VARIATION AMONG CATEGORIES
a	All Resins	Matrix (STY-DVB), (Acrylic), (Phenolic) (Epoxy), (Aliphatic)	5.18	.0089	60.9
b	WBA Resins	Matrix (STY-DVB), (Acrylic), (Phenolic) (Epoxy), (Aliphatic)	6.18	.0188	70.1
c	All Resins	Matrix (Nitrogen in), (Nitrogen out)	12.6	.0025	56.7
d	WBA Resins	Matrix (Nitrogen in), (Nitrogen out)	15.1	.0030	70.7
e	All Resins	Functionality (Poly), (Tertiary), (Quat.)	1.77	.2000	11.0
f	WBA Resins	Functionality (Poly), (Tertiary)	2.26	.1600	17.8
g	All Resins	Matrix * Functionality (All Combinations of Matrix and Functionality)	18.9	.0000	89.3
h	WBA Resins	Matrix * Functionality (All Combinations of Matrix and Functionality)	17.4	.0033	91.1
i	All Resins	Porosity (Micro), (Macro), (Iso)	4.32	.0316	37.8
j	WBA Resins	Porosity (Micro), (Macro)	12.6	.0053	66.5
k	SBA Resins	Porosity (Micro), (Macro), (Iso)	.211	.82	0.0
l	Type I SBA Resins	Porosity (Gel or Macro), (Iso)	.362	.60	0.0
m	Gel & MR SBA Resins	Type (I, Gel or MR), (II, Gel or MR)	.147	.73	0.0

to explain the preference of the zeolite, clinoptilolite for univalent ions like NH_4^+ by observing that bivalent ions could not remain stable in ion exchangers where the fixed charge sites were relatively far apart. This distance of separation may or may not be related to ion exchange capacity. In synthetic, organic, ion-exchange polymers like corsslinked polystyrene, one would expect the distance of separation between charged sites to be a function of capacity which would in turn be positively related to sulfate/nitrate selectivity. This distance between charged nitrogen atoms is expected to be randomly distributed with a mean dependent on the total number of sites per unit volume. Such is not the case with resins made from polyamine monomers, like diethylene-triamine when the mean distance of separation between nitrogen atoms (ion-exchange sites) in the polymer is expected to be highly correlated with the original separation distance in the monomer. Consider for example, a polyacrylic polyamine resin made from acrylic acid and diethylene-triamine [60].



Note that, symbolically at least, this particular amine monomer remains relatively unchanged as it provides crosslinking between acrylic acid chains; the active-nitrogen atoms remain separated by two methylene groups. For a similar effect, see the structure of phenol-formaldehyde-polyamine resins in the

section on "Structure of Ion Exchange Resins."

The experimental results did prove that sulfate selectivity, as measured by $\ln \alpha_N^S$, was predictable with modest reliability from capacity data for resins ($r = .54$, Figure F2). However, capacity cannot be used to predict sulfate selectivity for strong base resins ($r = .12$, Figure F3). The important conclusion to note however is that nitrogen position (in or out of the matrix) is a much better prediction of $\ln \alpha_N^S$ ($r = 0.96$, Figure 7) than is capacity, or any other variable for that matter. The relevant, simple regression equations for all resins are:

$$\ln \alpha_N^S = 2.48 \text{ CAPACITY} - 1.60 \quad (\text{Figure F1}) \quad (25)$$

$$\ln \alpha_N^S = 3.34 \text{ N2POSITN} + 1.05 \quad (\text{Figure 7}) \quad (26)$$

and for WBA resins:

$$\ln \alpha_N^S = 1.77 \text{ CAPACITY} + 0.369 \quad (\text{Figure F2}) \quad (27)$$

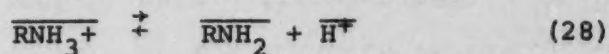
the fact that $\ln \alpha_N^S$ isn't related to capacity for strong base resins is probably due to (1) the relatively narrow range of capacities available for study -- 1.02 to 1.66 meq/ml and (2) stearic hindrance and poor polarizability of the quaternary-amine molecule which may be large enough to prevent closer approach of adjacent functional groups present with the highest capacity resins compared to the lowest.

Apparently, the distances of separation and the sizes of functional groups in resins with nitrogen in the matrix (epoxies, acrylics, phenolics) are such that stable, electrostatic bonds are formed with the divalent-sulfate ion making these resins highly sulfate selective at this level of total concentration (0.005N).

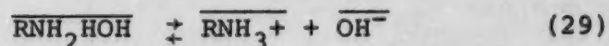
From the WBA correlation matrix Table F2 (Appendix) we have observed that nitrate/chloride selectivity is unrelated to capacity but is significantly, negatively correlated with nitrogen in the matrix. Figure 8 is the regression line/scatter plot of this latter relationship which is significant but only modestly so ($r = -.65$) compared to the same correlation for sulfate/nitrate selectivity ($r = .96$) just discussed. Some possible reasons for this negative correlation will be discussed in the section on crosslinking.

Effect of pKa on α_N^S and α_{Cl}^N --

The pKa of a resin is a measure of its tendency to keep a hydrogen ion, or alternatively, to give up a hydroxide ion.



or



The high affinity that WBA resins have for hydroxide ions ($pK_a = 8$) as compared to the very low affinity SBA resins have for hydroxide ions ($pK_a > 13$) is the reason for the easy and efficient regeneration of WBA resins by both strong (NaOH) and weak bases (NH_4OH) alike. The disadvantage accompanying this ease of regeneration is that the solution to be deionized must be sufficiently acidic to preclude the association of the protonated amine with the much preferred hydroxide ion instead of the ion it is desired to remove, e.g., sulfate chloride or nitrate. Insignificant concentrations of hydroxide ions existed in the isotherm experiments performed here as acids were utilized to provide the exchanging ions. Resulting liquid phase pH's were near 2.3 (.005N). Furthermore, Boari [13] showed that the sulfate/chloride separation factor was independent of pH when the total resin capacity was constant i.e., at pH's several units below the resin pKa.

In the absence of hydroxide ion interference, there would seem to be no theoretical reason why pKa should be associated with sulfate/nitrate or nitrate/chloride selectivity except through some correlation of pKa with a selectivity-relevant variable like "R" group size. This particular, secondary correlation effect does appear to have occurred. Figure F4 (Appendix) depicts a statistically significant negative correlation ($r = -.64$) between $\ln \alpha_N^S$ and pKa where it appears that the strong-base (pKa = 13) resins determine the existence of any correlation at all. Considering the same relationship for weak base resins only (Figure F5, Appendix) we see an entirely different picture; here sulfate nitrate selectivity is slightly, positively correlated with pKa, but the relationship isn't statistically significant i.e., pKa gives no information about the sulfate selectivity of WBA resins in general. There is however a curious downward trend of the data points at the top of Figure F4. Careful examination of the dataset revealed that all those points represented non-polystyrene resins. Figure F6 (Appendix) illustrated $\ln \alpha_N^S$ and pKa for non-polystyrene resins only, and that is new, useful information for a specific subclass of resins not a secondary correlation as is the one depicted in Figure F4 covering all the resins but yielding no new information because pKa is highly correlated with "R" group size (Table F2, $r = .80$) and we already know theoretically and empirically that quaternary amines should and do have relatively low sulfate (divalent-ion) selectivity.

A similar secondary correlation appears in Figure F7 where $\ln \alpha_{Cl}^N$ is plotted vs pKa for polystyrene resins only; again quaternary resins determine the relationship and no new information is gained. The pKa of a resin appears to have no real, causal effect on sulfate/nitrate or nitrate/chloride selectivity except for non-polystyrene WBA resins and would not be expected to be included in an efficient equation predicting selectivity from resin properties.

SCATTER PLOT

N = 29 OUT OF 32 9.LOG S N VS. 12.N2POSITN

LOG S/N
4.9200

4.0433

3.1666

2.2899

1.4132

.53649

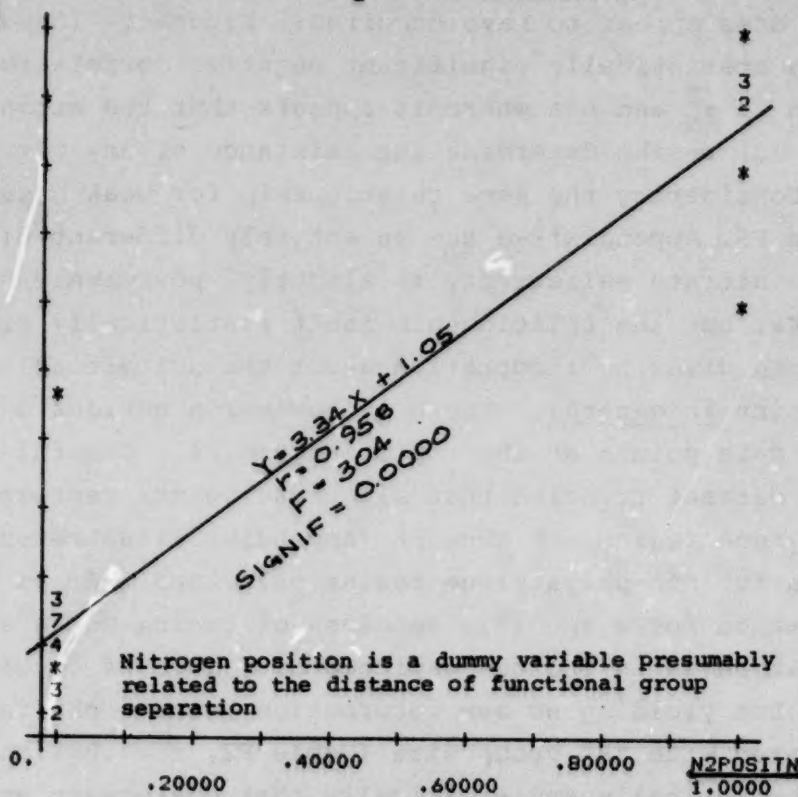


FIGURE 7

SCATTER PLOT WITH LINEAR REGRESSION EQUATION

$\ln \alpha_N^S$ vs. NITROGEN POSITION

FOR

WEAK AND STRONG BASE RESINS

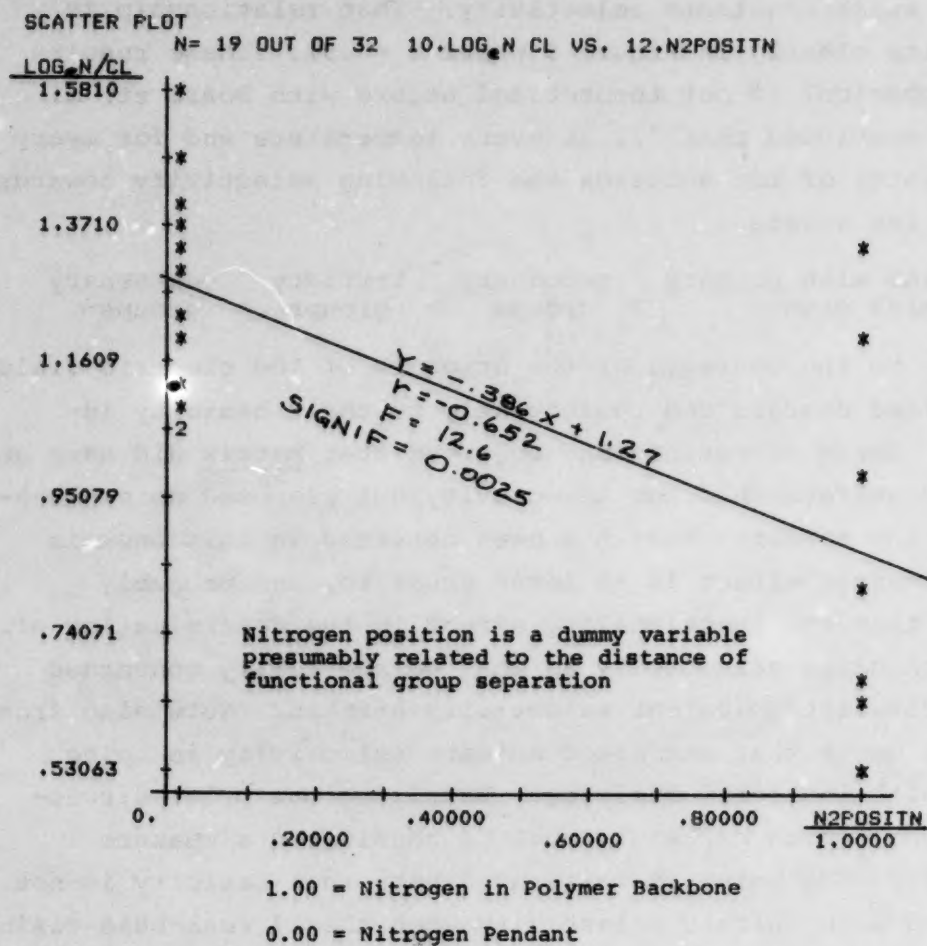


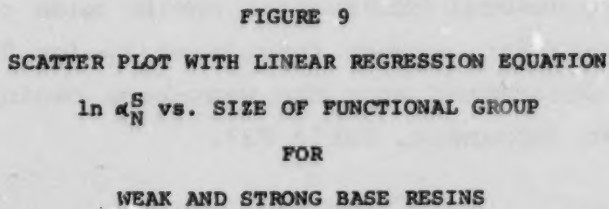
FIGURE 8
SCATTER PLOT WITH LINEAR REGRESSION EQUATION
 $\ln \alpha_{Cl}^N$ vs. NITROGEN POSITION
FOR
WEAK AND STRONG BASE RESINS

Effect of Functionality on α_N^S and α_{Cl}^N

The expected effect of functionality on sulfate selectivity did materialize -- the larger the "R" group the lower the relative sulfate/nitrate selectivity. That relationship is shown quite clearly in Figure 9 where $r = .91$. These results are in empirical if not theoretical accord with Boari et. al [13] who concluded that "...at every temperature and for every bulk salinity of the solution the following selectivity towards the $SO_4^{=}$ ion exists

resins with primary secondary Tertiary Quaternary
amino groups > groups > groups > groups

According to the decrease of the strength of the electric field of the fixed charges and consequently to their basicity increase." These investigations observed that matrix did have an effect on sulfate/chloride selectivity but proposed no explanation for the effect. What has been observed in this work is that the matrix effect is at least equal to, and probably greater, than the functionality effect in the determination of sulfate/chloride selectivity as what we are really concerned with is divalent/univalent selectivity effects. Note also from the above quote that increased sulfate selectivity is being equated with increased basicity. Recalling our prior discussion of pK_a , which certainly must be considered a measure of basicity; the point is reiterated here that basicity is not correlated with sulfate selectivity when the 13 weak-base resins are considered (pK_a range = 6.8 thru 11.1; Figure F5). It is only when the quaternary resins are included in or when the polystyrene resins are excluded from the regression analysis that statistically significant relationships are obtained (Figures F4 & F6). This it has been pointed out is a secondary effect, the size of the functional group being of primary importance. Boari's results and ours are still in accord, but that is due to the relative sizes of the functional groups not their basicity, which is unrelated to size among the weak base resins considered. Basicity is, in fact, not monotonically



related to functionality even in simple alkylamine monomers as the listing below (Reference 34 p. 5-15) illustrates:

TABLE 11. pKa's OF ALKYLAMINES IN WATER AT 25°C

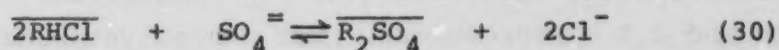
Amine Functionality	Amine	pKa
<u>Methylamines</u>		
Primary	$(\text{CH}_3)\text{NH}_3^+$	10.62
Secondary	$(\text{CH}_3)_2\text{NH}_2^+$	10.77
Tertiary	$(\text{CH}_3)_3\text{NH}^+$	9.80
Quaternary	$(\text{CH}_3)_4\text{NOH}$	>13.0 (est)
<u>Ethylamines</u>		
Primary	$(\text{C}_2\text{H}_5)\text{NH}_3^+$	10.63
Secondary	$(\text{C}_2\text{H}_5)_2\text{NH}_2^+$	10.93
Tertiary	$(\text{C}_2\text{H}_5)_2\text{NH}^+$	10.72
Quaternary	$(\text{C}_2\text{H}_5)_4\text{NOH}$	>13.0 (est)

For these methylamine and ethylamine monomers there is no clear basicity trend except that the quaternary amines are stronger than all the others for which no simple trend exists. The same general observation can be made regarding the lack of correlation between functionality (or "R" size) and the resin pKa's determined from the weak-base resin, titration curves; $r = .0155$ (Appendix, Table F2).

The summary argument for the size of the functional group being more important than its basicity in determining sulfate selectivity is

- (1) High divalent-ion (sulfate) selectivity clearly depends on functionality the order of α_N^S being:
primary > secondary > tertiary > quaternary
- (2) The size of functional groups can be ranked in the order:
primary < secondary < tertiary < quaternary
- (3) The basicity of functional groups in resins (and aliphatic amine monomers) can only be ordered as:
quaternary > tertiary, primary, secondary

Before discussing nitrate/chloride selectivity in some detail it is appropriate to study the physicochemical model of selectivity used by Boari [13] and attributed to Eiseman [43] the components of which have been discussed elsewhere by Reichenberg [103] and others [60, 38, 39, 69, and 26]. Energetically, the ion-exchange reactions may be accounted for by two distinct physiochemical processes: (1) the partial or total destruction of the hydrated structure of the counterion in dilute aqueous solution, and (2) electrostatic bonding of counterion to the resin structure (coion). Considering the binary ion exchange of sulfate and chloride:



Boari calculated that the electrostatic energy term was predominant over the hydration term when the overall change in standard free energy of the system was taken to be:

$$\begin{aligned} (\Delta G_{ex}^\circ)_{SO_4/Cl} = & (\Delta G_{Cl} - 1/2 \Delta G_{SO_4})_{\text{hydration}} \\ & - (\Delta G_{Cl} - 1/2 \Delta G_{SO_4})_{\text{electrostatic}} \quad (31) \end{aligned}$$

In fact, it is generally true, as has already been discussed, that in dilute solution (<.06N), ion exchangers prefer the ion with the highest valence, an observation also indicating predominance of the electrostatic term. When considering ions of

similar valence, however, the electrostatic contribution to the overall free energy change is not expected to outweigh the hydration contribution. This appears to be the case with nitrate/chloride exchange.

Effect of Functional Group on Nitrate/Chloride Selectivity

The scatter plot of $\ln \alpha_{Cl}^N$ vs "R" group size is Figure F8 where it is seen that no significant ($r = .25$) linear relationship exists. There do appear to be some trends however when the polystyrene resins (circled data points) are separated from the others: (1) the polystyrene resins have generally higher nitrate selectivity and (2) the tertiary polystyrene resins generally have the highest nitrate/chloride selectivity. The former observation is a reaffirmation of the previous finding that nitrogen out of the matrix (polystyrene) produces generally higher nitrate preference wrt chloride (Figure 8).

Effect of Relative Degree of Crosslinking on Nitrate/Chloride Selectivity

Recall that the categorical variable, porosity, having the stratifications: isoporous, microporous and macroporous was converted to the dummy variable XLINKING i.e., the relative degree of crosslinking with values of 0.5 = isoporous, 1.0 = microporous and 2.0 = macroporous. For non-polystyrene resins, nitrate/chloride selectivity is positively correlated (Figure 10, $r = .89$) with the relative degree of crosslinking - macroporous resins tending to have higher nitrate selectivity than microporous resins. For polystyrene resins no such relationship exists (Figure 11, $r = .33$). Consequently, when all resins are considered, only a modest correlation ($r = .45$) results which is barely significant at the .06 level. In summarizing the effects of both matrix and crosslinking the following trends are observed:

High nitrate/chloride preference is indicated by:

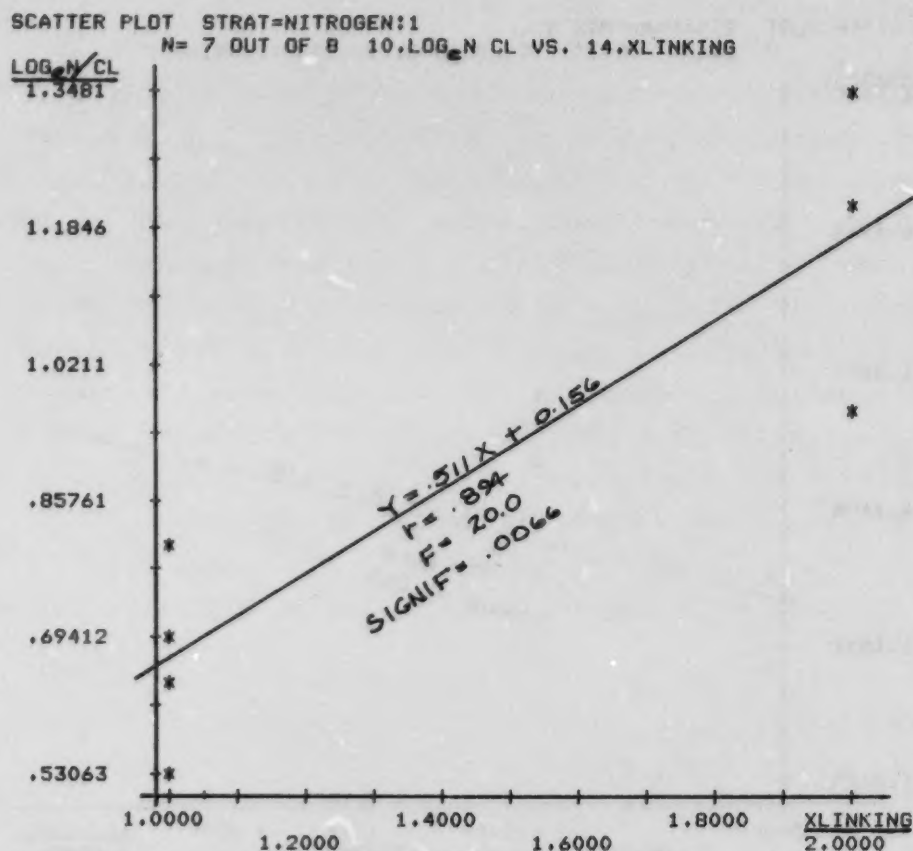


FIGURE 10
SCATTER PLOT WITH LINEAR REGRESSION EQUATION
 $\ln a_{N/CL}^N$ vs. RELATIVE DEGREE OF CROSSLINKING
FOR
NON-POLYSTYRENE RESINS

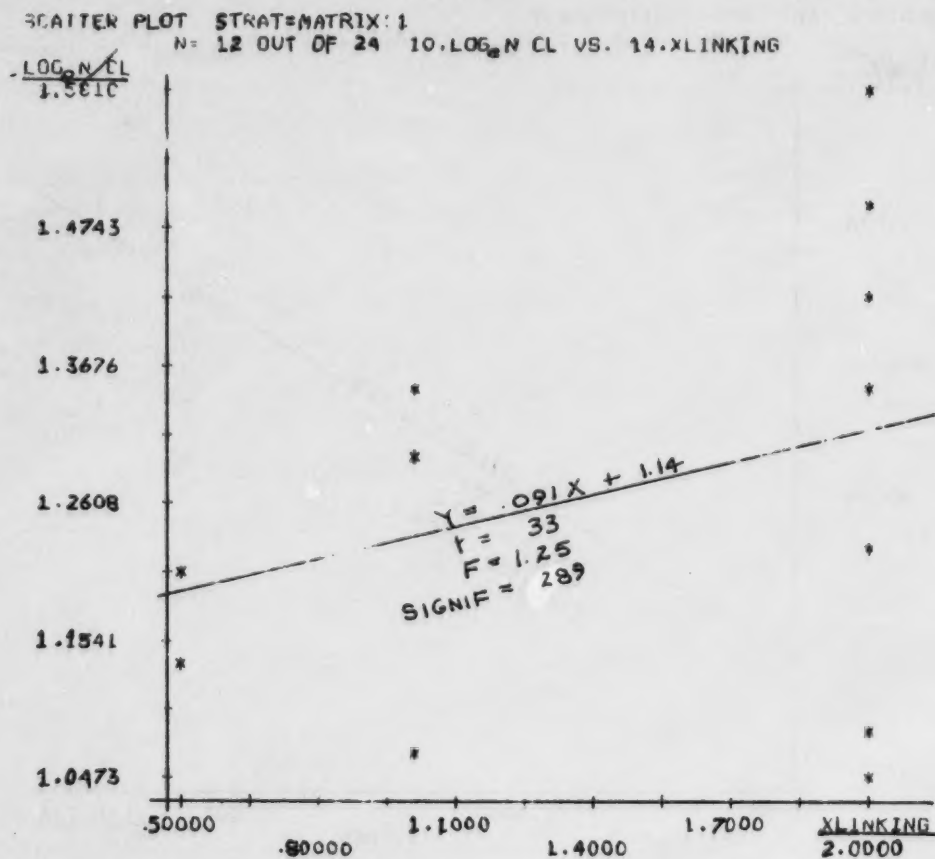


FIGURE 11
SCATTER PLOT WITH LINEAR REGRESSION EQUATION
 $\ln \alpha_{C1}^N$ vs. RELATIVE DEGREE OF CROSS LINKING
FOR
POLYSTYRENE RESINS

- (1) polystyrene resins in general
- (2) tertiary > quaternary (for polystyrene resins only)
- (3) macroporous > microporous (for non-polystyrene resins only)

The nitrate/chloride preferences which these resins exhibit are rather difficult to explain in terms of the expected changes in free energies of ionic hydration and electrostatic interaction.

Three parameters indicative of the order of hydration energy:

(1) effective ionic radius in aqueous solution, (2) ionic activity coefficient and, (3) limiting equivalent ionic conductance are given in the tables below. For each parameter, the ions are listed in the order of expected preference by the resin phase in dilute solution (<0.05N).

TABLE 12 [34]. EFFECTIVE IONIC RADII IN
AQUEOUS SOLUTION: A, 25°C

(also referred to as
Hydrated Ionic Radii
and
Debye-Hückel Ion-Size Parameter, $\text{\AA}$)

Chloride	=	3.0
Nitrate	=	3.0
Sulfate	=	4.0
Bicarbonate	=	4.0

TABLE 13 [34]. INDIVIDUAL IONIC ACTIVITY COEFFICIENTS (γ_i)

of
Ions in Water at 25°C, .005N
Calculated from:

$$-\log \gamma_i = \frac{AZ_i^2 \sqrt{I}}{1 + Ba\sqrt{I}}$$

$$\text{where: } I = 0.5 \sum_i C_i Z_i^2$$

Bicarbonate	= .927
Chloride	.925
Nitrate	.925
Sulfate	.693

TABLE 14 [34]. LIMITING, EQUIVALENT, IONIC CONDUCTANCE
IN AQUEOUS SOLUTION AT 25°C

mho · cm²/equivalent

1/2 sulfate	= 80.00
chloride	= 76.35
nitrate	= 71.40
Bicarbonate	= 44.50

Actually, ionic conductance is a measure of both the hydration and electrostatic energy effects; the rate at which an ion moves through water in an electric field is influenced among other things by its hydration shell and the charge it carries. Conductance does correctly predict that sulfate should be the most preferred and bicarbonate the least preferred but incorrectly predicts as do the other two parameters that chloride should be equally or more preferred than nitrate.

That polystyrene resins and relatively highly crosslinked

resins exhibit the highest nitrate/chloride selectivity may have to do indirectly with the water content of the resins - these categories of resins being expected to contain relatively less water due to their hydrophobic non-polar character.

Sulfate/Nitrate vs Nitrate/Chloride Selectivity

Considering all resins, low sulfate selectivity generally corresponds with low chloride selectivity. This was originally presumed to be a fortunate correlation; see Figure F9 where $r = -.53$ for $\ln \alpha_N^S$ vs $\ln \alpha_{Cl}^N$. Among the weak base resins the correlation is even higher with $r = -.67$ (Table F2). It is presumed to be fortunate because minimizing the sulfate selectivity also tended to minimize the chloride selectivity i.e., the effects of nitrogen position, functionality and porosity on selectivity do not offset one another; however, as we shall see later, moderate to high sulfate selectivity actually improves the chemical efficiency of the nitrate removal processes.

Sampling Bias: "R" Group Size vs Nitrogen Position

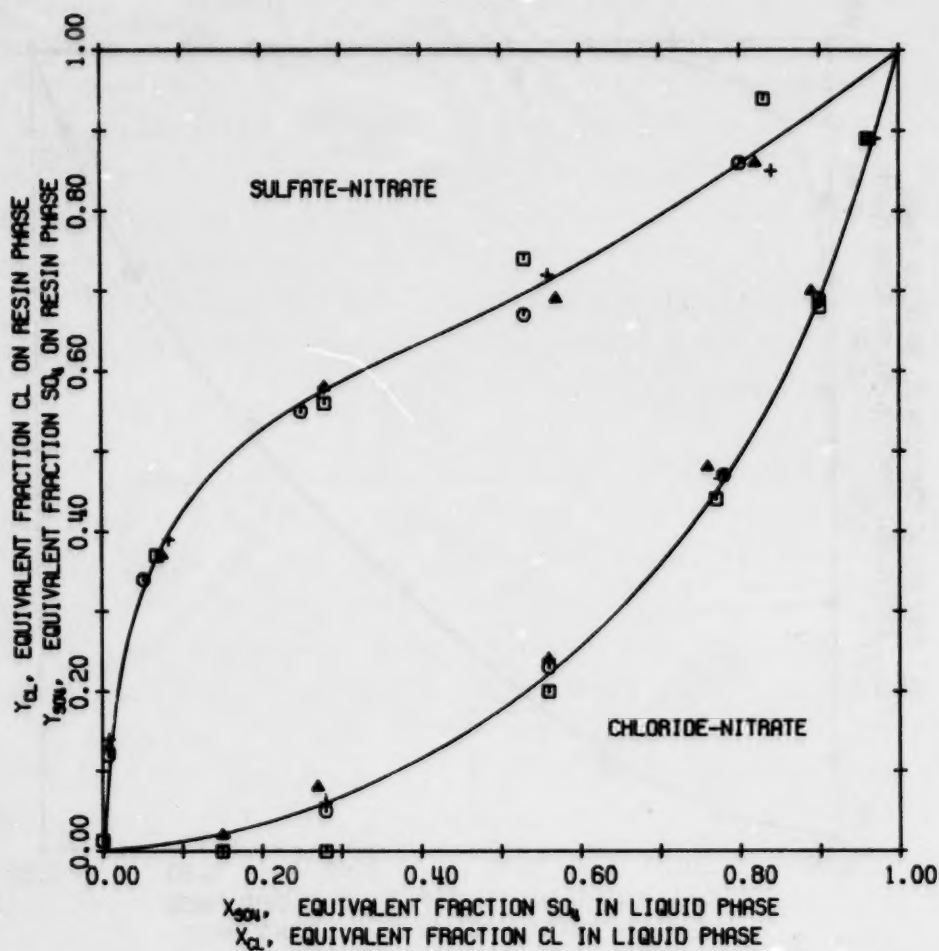
The previous discussion has emphasized the importance of functionality and nitrogen-in-or-out of the matrix in determining selectivity. Unfortunately, for this particular sampling of resins, these two variables were highly correlated making it more difficult to see intuitively which factor was most important; see Figure F10 where $r = -.82$ for "R" Group Size vs Nitrogen Position. There is some fundamental reason for this correlation; all the quaternary amine resins have nitrogen out of the matrix and this author is unaware of the existence of a monofunctional quaternary amine resin where nitrogen is part of the continuous structure¹.

¹Helfferich [60] mentions a polycondensation polymer of polyethyleneamine and epichlorohydrin, but this resin has tertiary and secondary amines mixed with the quaternary groups. Another possible exception, Amberlite IRA 458, an acrylic gel Type 1 strong-base anion resin was not evaluated in this work.

In spite of this fundamental problem, the correlation could have been made less significant had there been more tertiary amine resins with nitrogen in the matrix (like Amberlite IRA-68, acrylic-tertiary) and more polyamine resins with nitrogen out of the matrix (like Amberlite IR-45, STY-DVB-polyamine). The addition of such resins to the data set would have improved the reliability (significance) of the correlations but would not have changed their validity. This assumes, of course, that all resins having the same functionality and matrix behave essentially the same with respect to selectivity - a fact which has been observed and is amply demonstrated by the composite isotherms (Figures 12-17).

Selection of Regression: The Final Statistical Result

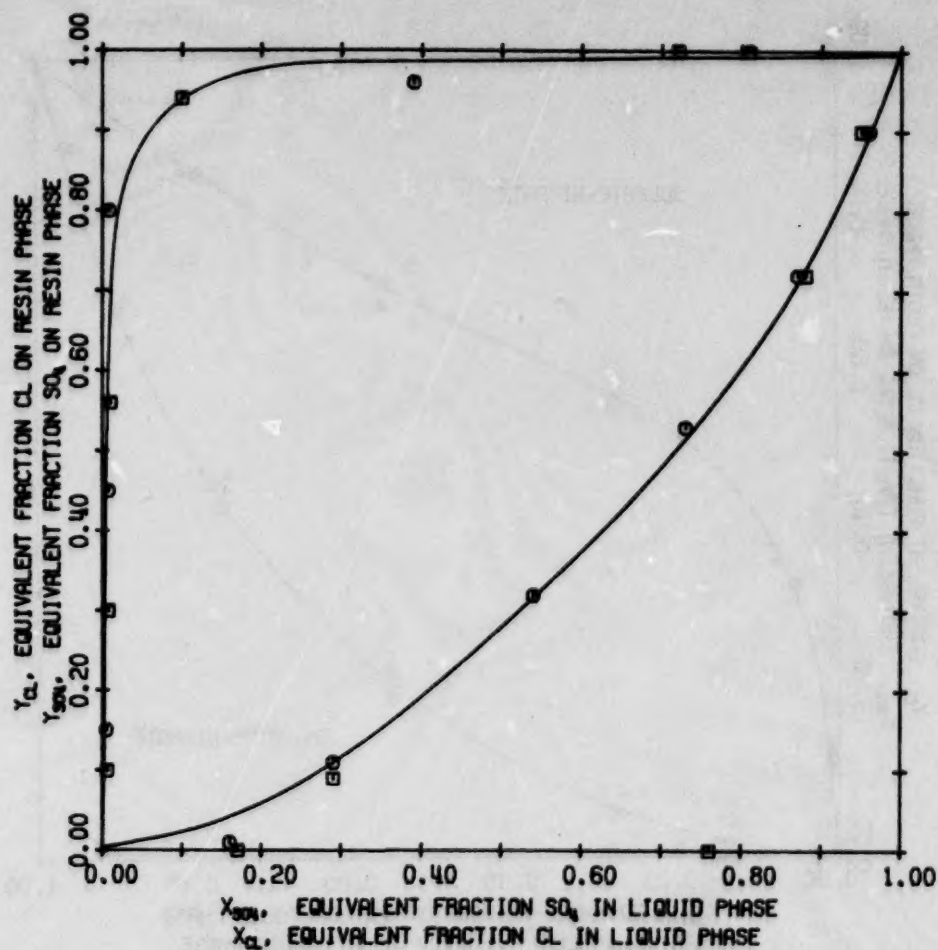
Having established which independent variables were most important in determining selectivity and having created the necessary interval-scale dummy variables to represent the important categorical variables, the task remaining was to incorporate these into a simple, efficient predictive equation. The selection of regression technique [42, 48] was used to accomplish this objective. It is essentially the optimization of a multiple regression analysis. The dependent variable to be predicted is chosen along with the independent variables and the desired levels of significance for inclusion and rejection of the various independent variables. The program computes the individual, simple, linear-regression coefficients (r 's) for each independent variable then chooses the highest one which is significant at or below the level specified. The partial correlation coefficients are then computed for the remaining variables i.e., the ability of each of the remaining variables to account for the remaining variance is determined. Whichever one of these has the highest, partial correlation coefficient is then incorporated into the now multiple-regression equation but only if it improves the multiple correlation coefficient (R) at or below the second level of significance



WEAK BASE ANION RESINS 1, 5, 8 & 12
MACROPOROUS RESINS, STYRENE-DVB MATRICES
TERTIARY AMINE FUNCTIONALITY

- = RESIN NO. 1, AMBEALITE IRA 93
- = RESIN NO. 5, DOWEX MWA-1
- △ = RESIN NO. 8, DUOLITE ES-368
- + = RESIN NO. 12, IONAC AFP 329

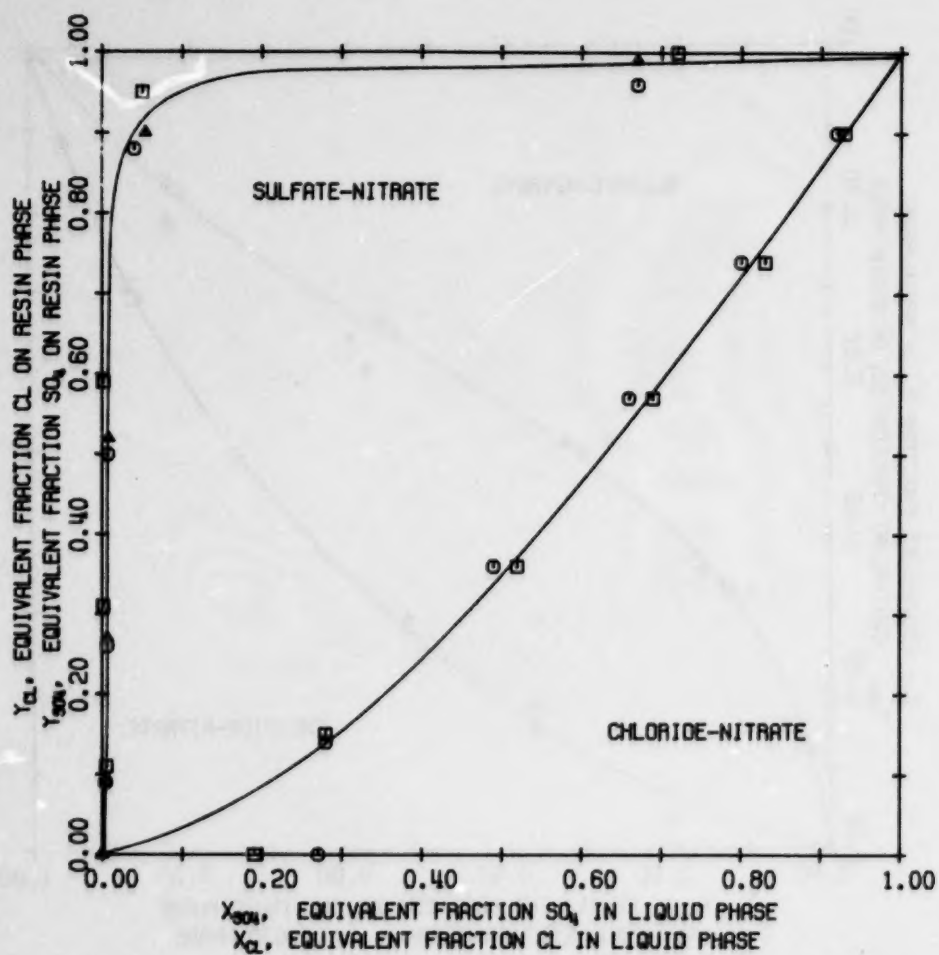
FIGURE 12
COMPOSITE ISOTHERMS, 25° C, 0.005 N



WEAK BASE ANION RESINS 6 & 9
 GRANULAR, MACROPOROUS RESINS, PHENOLIC MATRICES
 POLYAMINE FUNCTIONALITY

□ = RESIN NO. 6, DUOLITE A7
 ○ = RESIN NO. 9, DUOLITE ES-561

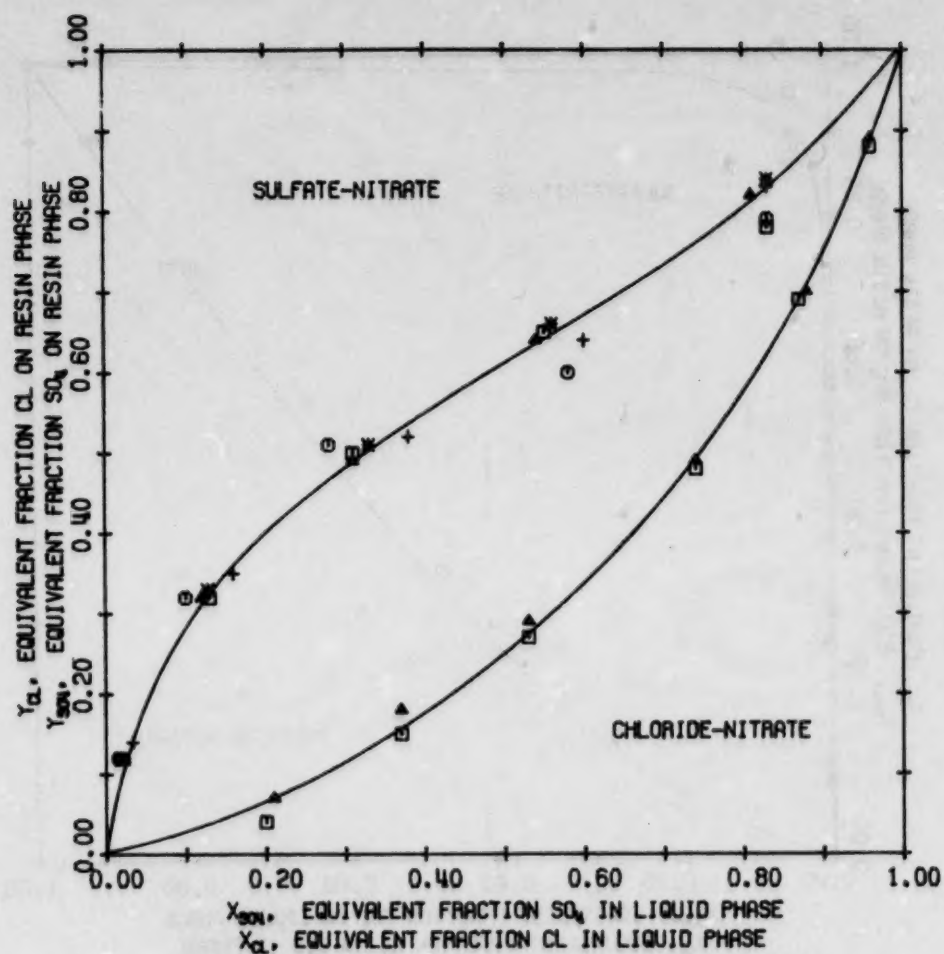
FIGURE 13
 COMPOSITE ISOTHERMS, 25° C, 0.005 N



WEAK AND INTERMEDIATE BASE ANION RESINS 4, 7 & 13
 GEL RESINS, EPOXY-AMINE MATRICES
 POLYAMINE FUNCTIONALITY

□ = RESIN NO. 4, DOWEX WGR
 ○ = RESIN NO. 7, DUOLITE A-340
 ▲ = RESIN NO. 13, IONAC A-305

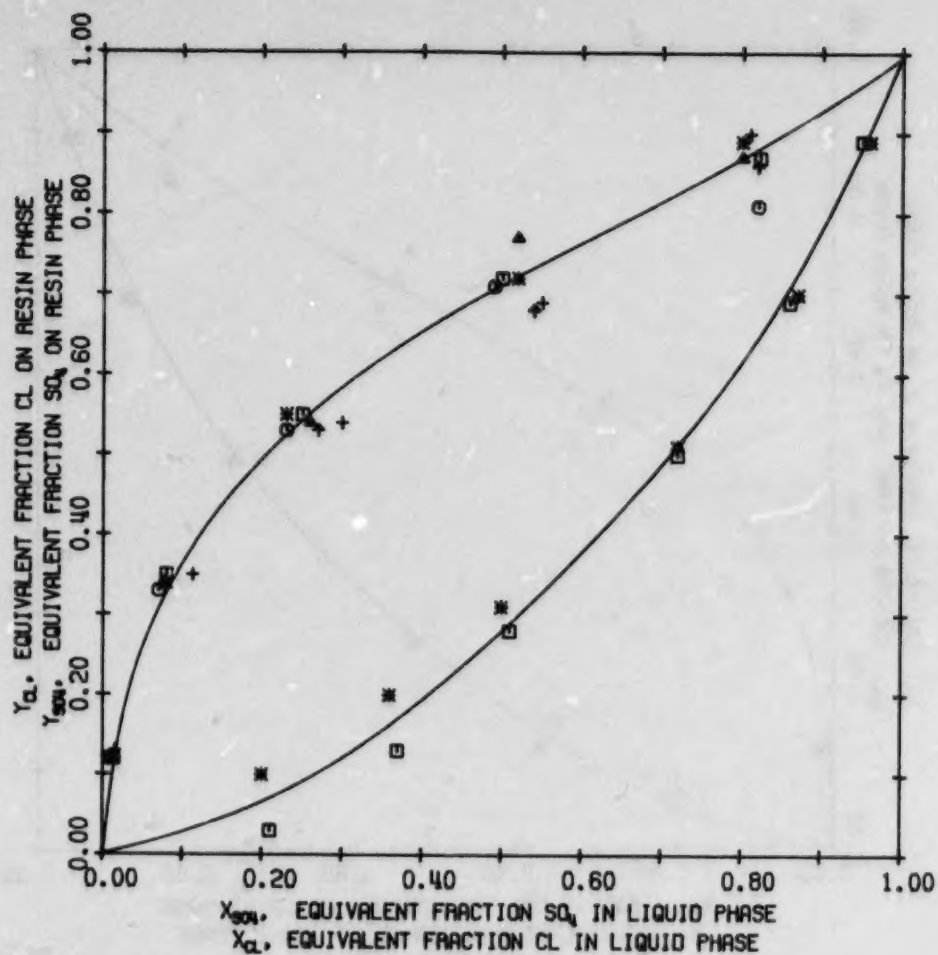
FIGURE 14
 COMPOSITE ISOTHERMS, 25° C, 0.005 N



STRONG BASE ANION RESINS 15, 17, 21, 27 & 32
GEL AND MACROPOROUS RESINS, STYRENE-DVB MATRICES
TYPE I, QUATERNARY AMINE FUNCTIONALITY

- = RESIN NO. 15, AMBERLITE IRA-400
- = RESIN NO. 17, AMBERLITE IRA-900
- △ = RESIN NO. 21, DOWEX SBA
- + = RESIN NO. 27, IONAC ASB-1
- * = RESIN NO. 32, IONAC AFP-100

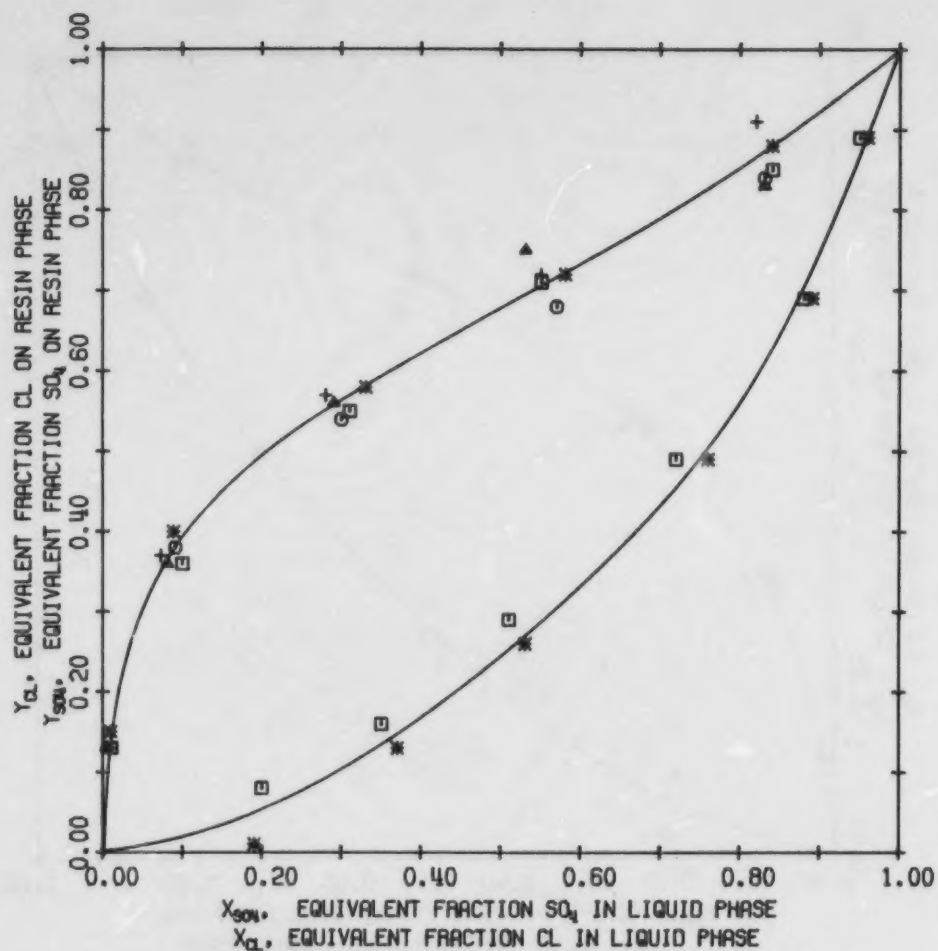
FIGURE 15
COMPOSITE ISOTHERMS, 25° C, 0.005 N



STRONG BASE ANION RESINS 16, 19, 22, 24, 28 & 30
 "IMPROVED POROSITY" GEL RESINS, STYRENE-DVB MATRICES
 TYPE I, QUATERNARY AMINE FUNCTIONALITY

- = RESIN NO. 16, AMBERLITE IRA-402
- = RESIN NO. 19, DOWEX SBR-P (21-K)
- △ = RESIN NO. 22, DOWEX 11
- ⊕ = RESIN NO. 24, DOWEX A-101-D
- * = RESIN NO. 28, IONAC A-641
- ⊙ = RESIN NO. 30, IONAC ASB-1P

FIGURE 16
 COMPOSITE ISOTHERMS, 25° C, 0.005 N



STRONG BASE ANION RESINS 14, 18, 20, 23 & 29
 GEL AND MACROPOROUS RESINS, STYRENE-DVB MATRICES
 TYPE II, QUATERNARY-AMINE FUNCTIONALITY

□ = RESIN NO. 14, AMBERLITE IAA-910 (MA)
 ○ = RESIN NO. 18, AMBERLITE IAA-410
 △ = RESIN NO. 20, DOWEX SAR
 + = RESIN NO. 23, DUOLITE A-102-D
 * = RESIN NO. 29, IONAC ASB-2

FIGURE 17
 COMPOSITE ISOTHERMS, 25° C, 0.005 N

specified. The procedure is repeated until there are either no significant partial correlations remaining or no significant improvement in multiple R is possible. An example output for the selection of regression of N2POSITN, RSIZE, CAPACTIY AND XLINKING on $\log_e \alpha_N^S$ for WBA resins is included in Appendix F for review. A similar example for the selection of regression of the same variables on $\log_e \alpha_{Cl}^N$ is also included in Appendix F. The resulting predictive equations are listed below with their associated statistical parameters.

Sulfate/Nitrate Selectivity for all Resins:

$$\ln \alpha_N^S = 2.30 \text{ N2POSITN} - 3.63 \text{ RSIZE} + 9.44 \quad (33)$$

$$R = 0.980$$

$$F = 317$$

$$\text{SIGNIF} = .0000$$

Sulfate/Nitrate Selectivity for WBA Resins

$$\ln \alpha_N^S = 2.03 \text{ N2POSITN} - 7.45 \text{ RSIZE} + 17.44 \quad (34)$$

$$R = .991$$

$$F = 261$$

$$\text{SIGNIF} = .0000$$

Nitrate/Chloride Selectivity for All Resins

$$\ln \alpha_{Cl}^N = -0.371 \text{ N2POSITN} + 0.206 \text{ XLINKING} + 0.962 \quad (35)$$

$$R = .772$$

$$F = 11.8$$

$$\text{SIGNIF} = .0007$$

Nitrate/Chloride Selectivity for WBA Resins

$$\ln \alpha_{Cl}^N = -0.413 \text{ N2POSITN} + 0.381 \text{ XLINKING} + 0.755 \quad (36)$$

$$R = .919$$

$$F = 24.6$$

$$\text{SIGNIF} = .0002$$

The usefulness of the equations for "all resins" is that they indicate the two most important variables out of the six possible which influence the selectivities of anion resins in general. For predictive purposes three additional equations are offered. They are based on the results of the analysis of variance tests. See Table 8.

$$\alpha_N^S = 1.82 \text{ for all Type I, Gel and MR SBA resins}$$

$$\alpha_N^S = 2.98 \text{ for all Type I, ISO; and Type II Gel and MR SBA resins}$$

$$\alpha_{Cl}^N = 3.14 \text{ for all SBA resins regardless of type or porosity}$$

Comparison of Predicted Selectivities to Measured Selectivities

Equations 39-43 were used to predict α_N^S and α_{Cl}^N for each representative type of resin. These predictions are compared to the average of the experimentally measured selectivities in Tables 15 and 16 following.

PHASE I RESULTS SUMMARY: ANION RESIN SELECTIVITY STUDIES

Thirty-two anion resins from four U.S. manufacturers were tested for nitrate, chloride, sulfate and bicarbonate selectivity; nitrate and chloride capacity, and organics bleed. Sulfuric, nitric and hydrochloric acid titration curves were constructed from equilibrium data for the weak base resins. The resins comprised a variety of combinations of matrix,

TABLE 15

PREDICTED AND MEASURED VALUES OF SULFATE/NITRATE SELECTIVITY: α_N^S

Resins	Resin Description	Predicted α_N^S *	Ave Measured α_N^S	% Error
1,5,8,12	STY-DVB, Tert. Amine, MR	3.08	3.08	0.
3	STY-DVB, Polyamine, Gel	12.7	12.7	0.
6,9	PEHNOL-HCHO-PA, Polyamine, MR	97	108	-10.
4,7,3	EPOXY-AMINE, Polyamine, GEL	97	109	-11.
11	ALIPHATIC-AMINE, POLYAMINE, GEL	97	54	+80.
2	ACRYLIC-AMINE, TERT.AMINE, GEL	23.4	23.4	0.
10	ACRYLIC-AMINE, POLYAMINE, MR	97	94	+3.
16,19,22				
24,28,30	STY-DVB, Quat. (I)Amine, ISO	2.98	2.99	0.
15,25,27	STY-DVB, Quat. (I)Amine, GEL	1.82	1.89	+4.
17,23	STY-DVB, Quat. (I) Amine, MR	1.82	1.74	+5.
18,26,				
23,29	STY-DVB, Quat.(II) Amine, GEL	2.98	2.94	+1.
14	STY-DVB, Quat.(II) Amine, MR	2.98	3.26	-9.

* Equations 39 and 41, 42 were used to calculate the WBA and SBA resin selectivities respectively.

With three equations, the sulfate/nitrate selectivities of 11 of the 12 relevant combinations of matrix, functionality, porosity and type are predicted to within + 11% in the extreme range of selectivities encountered: 1.8 to 109. By extrapolation, these equations should correctly predict (+ 11%) the selectivities of 24 of the 26 possible strong and weak-base resins. More importantly, only one equation is required to correctly describe (+ 11%) the sulfate/nitrate preferences of 6/7th of the weak-base resins: the primary subjects of this study.

On an individual resin basis, the three equations "correctly" predict α_N^S for 28 of the 29 resins evaluated and whose selectivities (α_N^S) vary over the wide range of 1.71 to 137.

TABLE 16

PREDICTED AND MEASURED VALUES OF NITRATE/CHLORIDE SELECTIVITY: α_{Cl}^N

Resins	Resin Description	Predicted α_{Cl}^N *	Ave Measured α_{Cl}^N	% Error
1,5,8,12	STY-DVB, Tert. Amine, MR	4.56	4.33	+5.
3	STY-DVB, Polyamine, Gel	3.11	3.89	-20.
6,9	PHENOL-HCHO-PA, Polyamine, MR	3.02	3.00	+1.
4,7	EPOXY-AMINE, Polyamine, GEL	2.06	1.85	+11.
11	ALIPHATIC-AMINE, POLYAMINE, GEL	2.06	2.25	-8.
2	ACRYLIC-AMINE, TERT. AMINE, GEL	2.06	1.89	+9.
10	ACRYLIC-AMINE, POLYAMINE, MR	3.02	3.85	-22.
16,28	STY-DVB, Quat. (I)Amine, ISO	3.14	3.22	-2.
21	STY-DVB, Quat. (I)Amine, Gel	3.14	2.90	+8.
17,32	STY-DVB, Quat. (I)Amine, MR	3.14	3.19	-2.
29	STY-DVB, Quat. (II)Amine, GEL	3.14	3.64	-14.
14	STY-DVB, Quat (II)Amine, MR	3.14	2.85	+10.

* Equations 40 and 43 were used to calculate the WBA and SBA resin selectivities respectively.

Here with two equations, the nitrate/chloride selectivities of all 12 relevant combinations of matrix, functionality porosity and type are predicted to within + 22% in the relatively narrow range of selectivities encountered: 1.85 - 4.33. Again, by extropolation, the selectivities of all 26 possible weak and strong base anion resins are expected to be correctly predicted by these equations (+ 22%).

One equation is necessary to predict (+ 22%) the α_{Cl}^N 's of all of the weak-base anion resins.

The two equations predict (+ 22%) the α_{Cl}^N values of all 19 of the resins for which nitrate/chloride selectivity was evaluated.

functionality, porosity, pKa, and capacity. Degree of cross linking had not been directly specified or determined, so it was related to porosity for data analysis. The following is a list of the ranges of the independent variables:

Matrix: STY-DVB, Acrylic, Aliphatic, Epoxy, Phenolic

Functionality: quaternary, tertiary, polyamine

Porosity: microporous, macroporous, isoporous

Capacity: 0.98 -- 2.54 meq/ml

pKa: 6.8 -- 13

See Table 3 for complete details on resins tests.

Sulfate was always preferred over nitrate by all the strong and weak-base resins tested which exhibited an extremely wide range of selectivities: $\alpha_N^S = 1.71$ to 137. Although these separation factors can strictly be applied only at 0.005N, it is expected that the selectivity trend will hold true for any anion resin tested with groundwaters having total dissolved solids up to at least 3000 ppm (0.06N as CaCO_3). See Figures A1-A32 (Appendix) and Variable Total Concentration Isotherms (Figure 19).

Nitrate was always preferred over chloride by all the anion resins tested although the range of preference was relatively narrow: $\alpha_{\text{Cl}}^N = 1.85$ -- 4.33, and, as expected, was not a function of total concentration. See the lowest isotherm of Figure 19.

The average separation factor, α_j^i , determined by the ratio of areas technique proposed here provided an adequate description of the resin preference for sulfate at constant α_N^S at a given total concentration (.005N) even though the least selective ($\alpha_N^S = 1.7$ to 3.7) resins yielded isotherms with inflection points and would have required empirical cubic equations for a good curve fit. See Figures A33 and A34 and Reference 100, Table 16-5. These more-or-less "S" shaped isotherms describe

the sulfate/nitrate behavior in tertiary and quaternary STY-DVB resins (Figures A1, A5, A8, A12 and A14-A32) of modest ($\alpha_N^S = 2.0 \text{ -- } 4.0$) sulfate preference as opposed to the apparently inflectionless isotherms of resins with high sulfate selectivity ($\alpha_N^S = 13\text{--}137$, Figures A2-A4, A7, A9, A11 and A13). It is proposed that the "S" shaped isotherms represent resins with sites of unequal preference for sulfate as verified by the generally higher preference (more convex curves) for sulfate at low equivalent fraction of that ion; see Helfferich [60] p. 183. The large tertiary and quaternary functional groups pendant on the polystyrene matrix may less frequently be close enough together to satisfy the divalent, sulfate ion than is the case with polystyrene - polyamine resins and non-polystyrene resins where the probability of the two requisite functional groups being close enough to satisfy divalency is expected to be much greater.

A separate indication of unequal preferences between ions of dissimilar valence is exemplified by the differences among the titration curves for a given weak-base resin; see Figures B1-B12. None of the polyamine resins have discernible inflection points for HCl or HNO₃ whereas all but one (Figure B9) have definite inflection points for H₂SO₄ indicating the presence of sites of nearly equal affinity for divalent anions like sulfate but not for monovalent ions like chloride and nitrate. As expected, all these polyamine resins showed great affinity for sulfate over nitrate. The exceptional resin, Duolite ES-561 (Figure B9) had been manufactured in such a way so as to minimize the number of pendant amine groups (R. Anderson, Diamond, Shamrock Chemical Co., Personal Communication), a procedure which tended to produce fewer pairs of sites preferring divalent anions.

Briefly, resins with relatively low sulfate selectivity have modestly "S"-shaped isotherms explained by the tendency

of these resins to have sites with varying affinities for the divalent sulfate ion. Resins of high sulfate selectivity have smooth shaped isotherms explained by the expected preponderance of pairs of sites available for divalent ion interactions.

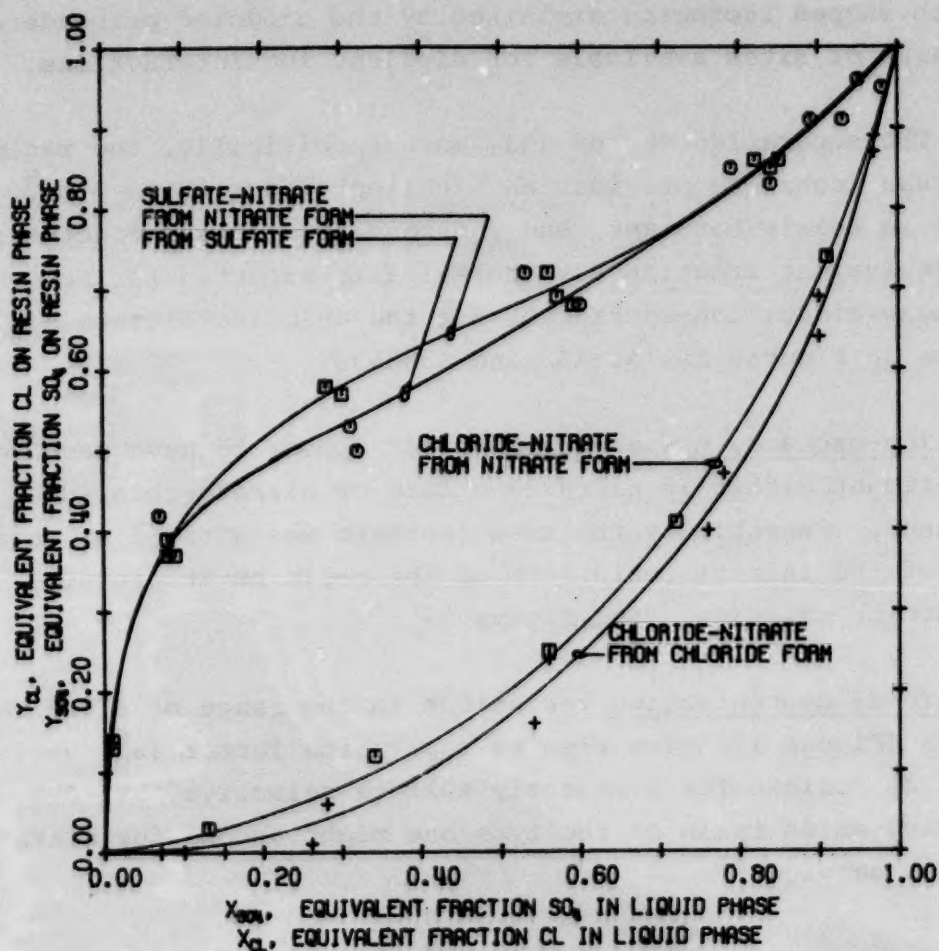
The separation factor and, more specifically, the ratio-of-areas technique provides an excellent description of α_{Cl}^N which is nearly constant, and independent of total concentration and equivalent fraction as theoretically expected for monovalent-monovalent, ion-exchange. See the chloride/nitrate isotherms in Figures 19, A1-A32 and A35-A36.

Ion-exchange hysteresis does not appear to have been very significant either in nitrate-sulfate or nitrate-chloride exchange. Essentially the same isotherm was arrived at regardless of the initial ionic form of the resin be it nitrate, sulfate or chloride. See Figure 18.

Total concentration variations in the range of 0.002 to 0.008N (Figure 19) gave rise to separation factor (α_N^S) variations as follows for a modestly sulfate selective, STY-DVB, tertiary amine resin of the type one might choose for nitrate removal service:

C_T	α_N^S
0.002 N	5.2
0.005 N	2.8
0.008 N	1.8

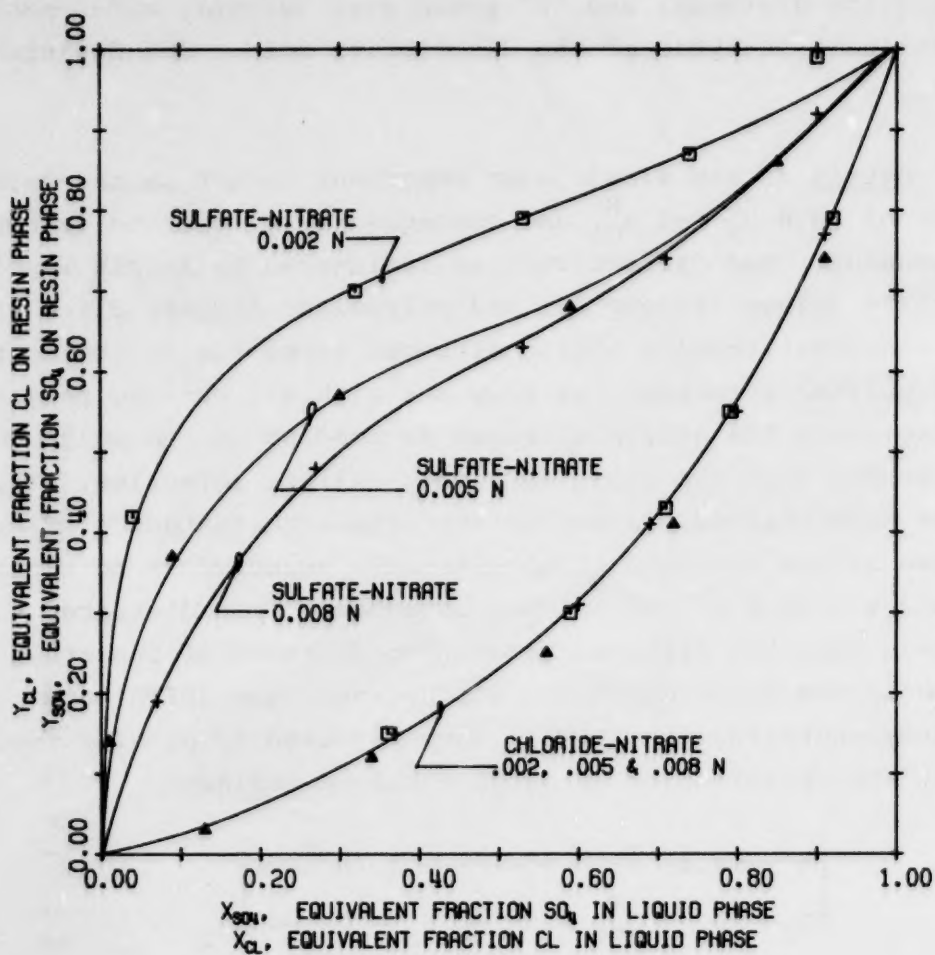
Statistical Analysis of the Phase I experimental data using analysis of variance, simple and multiple regression analyses; scatter plotting and selection (optimization) of regression yielded validated, predictive equations for sulfate/nitrate and nitrate/chloride selectivities. This was accomplished only after the relevant categorical variables, matrix and



WEAK BASE ANION RESINS 8 & 12
 DUOLITE ES-368, IONAC AFP-329
 MACROPOROUS RESINS, STYRENE-DVB MATRICES
 TERTIARY AMINE FUNCTIONALITY

□ = RESIN INITIALLY IN NITRATE FORM
 ○ = RESIN INITIALLY IN SULFATE FORM
 + = RESIN INITIALLY IN CHLORIDE FORM

FIGURE 18
 HYSTERESIS ISOTHERMS, 25° C, 0.005 N



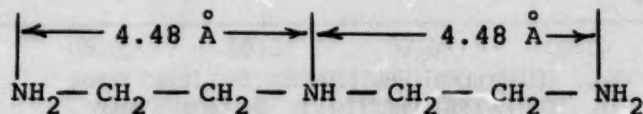
WEAK BASE ANION RESIN NO. 12
IONAC AFP-329
MACROPOROUS RESIN, STYRENE-DVB MATRIX
TERTIARY AMINE FUNCTIONALITY

□ = 0.002 N TOTAL CONCENTRATION
△ = 0.005 N TOTAL CONCENTRATION
+ = 0.008 N TOTAL CONCENTRATION

FIGURE 19
VARIABLE TOTAL CONCENTRATION ISOTHERMS, 25° C

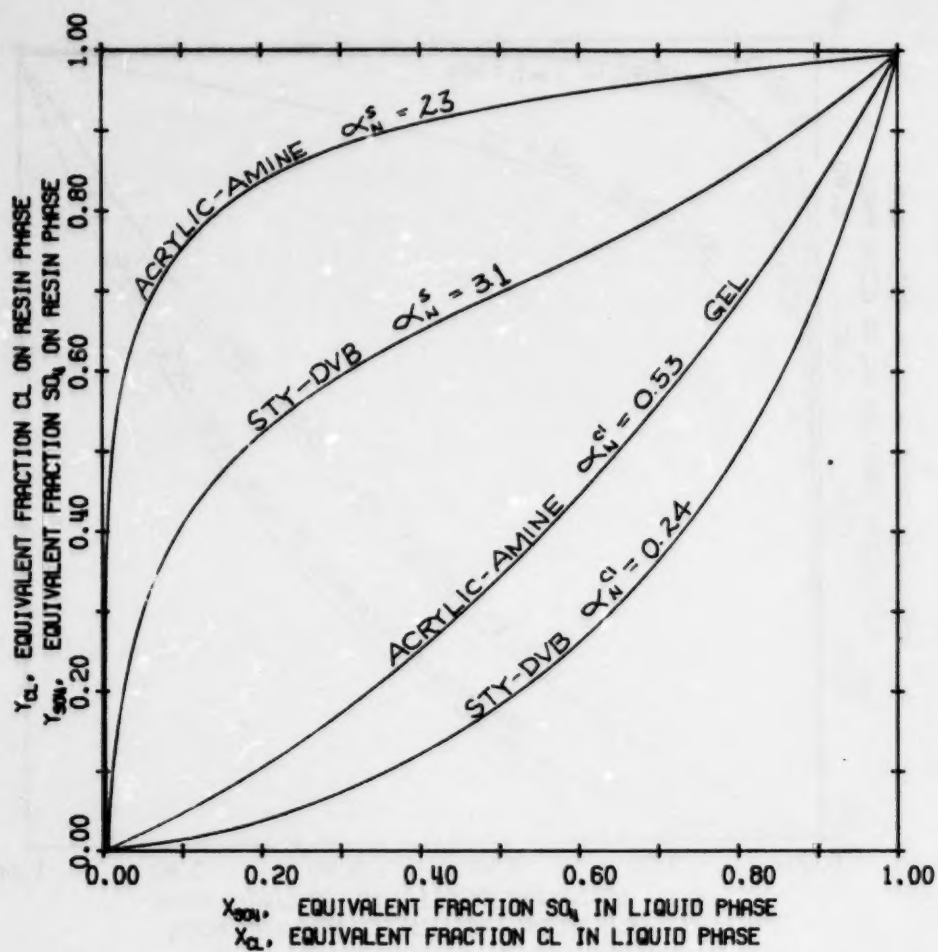
functionality, had been converted to interval scale, dummy variables: nitrogen position (N2POSITN -- related to coion separation distance) and "R" group size (RSIZE), after much preliminary analysis of the descriptive data. See Equations 37-43.

Matrix is the single most important factor in the determination of both α_N^S and α_{Cl}^N and consequently of nitrate selectivity in general. See "selectivity as influenced by matrix type" for tertiary amines (Figure 20) and polyamines (Figure 21). If the electrostatically active nitrogen atoms are in the continuous polymer structure, as they are with all but the polystyrene resins where the active nitrogen is pendant on the polymer structure, then the resin is highly sulfate selective. This, it is hypothesized, is due to the almost-guaranteed proximity of two active nitrogen atoms which are expected to be separated by about 4.48 Å in the polymer backbone. This distance, 4.48 Å, derives from the nitrogen separation distance of one ethylene group in the amine monomers, diethylenetriamine (DETA) and triethylenetetraamine (TETA), commonly used to provide functionality and crosslinking in anion exchange resins:



DETA

Fixed pairs of properly-spaced electrostatically-charged amines will tend to prefer single, divalent anions for both entropic and electrostatic reasons. With tertiary and quaternary amines pendant on a polystyrene matrix, the natural electroselectivity of multiple charged ions is reduced by the steric hinderance of the large functional groups and the lesser probability of their being properly spaced to interact with a divalent ion of fixed size like sulfate. Summarily the nitrate/sulfate selectivities



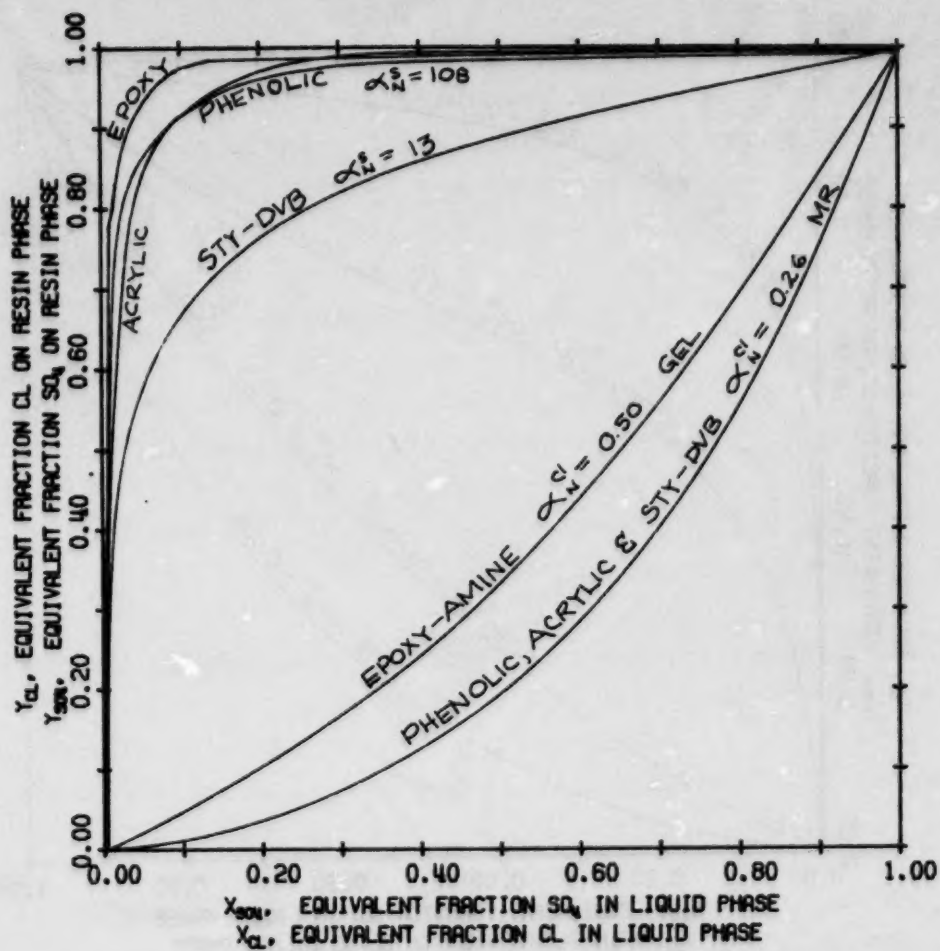
NO. 2; ACRYLIC AMINE, TERTIARY-AMINE RESIN, HCL CAP. = 1.42 MEQ./ML.

NO. 12; STYRENE-DVB, TERTIARY-AMINE RESIN, HCL CAP. = 1.26 MEQ./ML.

C₁ = 0.005 N.

T = 25° C

FIGURE 20
SELECTIVITY AS INFLUENCED BY MATRIX TYPE
(ALL TERTIARY-AMINE FUNCTIONALITY RESINS)



NO. 3; STYRENE-DVB, POLYAMINE RESIN, HCL CAP. = 1.76 MEQ./ML.
 NO. 4; EPOXY-AMINE, POLYAMINE RESIN, HCL CAP. = 1.53 MEQ./ML.
 NO. 6; PHENOL-HCHO, POLYAMINE RESIN, HCL CAP. = 1.67 MEQ./ML.
 NO. 10; ACRYLIC-AMINE, POLYAMINE RESIN, HCL CAP. = 2.59 MEQ./ML.
 $C_1 = 0.005 \text{ N.}$
 $T = 25^\circ \text{ C}$

FIGURE 21
 SELECTIVITY AS INFLUENCED BY MATRIX TYPE
 (ALL POLYAMINE FUNCTIONALITY RESINS)

(α_S^N not α_N^S) can be ordered as:

Polystyrene > non-polystyrene resins

That nitrogen in the continuous structure should be associated with low nitrate/chloride selectivity is not easily explained nor is the observation that nitrate is always preferred over chloride by all these anion resins. Their relative energies of hydration as indicated by calculated activity coefficients, and measured, limiting, ionic conductances, indicates that chloride should be favored. Electrostatically their charges are equal but structurally they differ; nitrate is larger [98, 67] and of greater polarizability than chloride [89], and nitrate is polyatomic-planar while chloride is monatomic-spherical [67]. The "water-structure-enforced, ion pairing" described by Diamond [38] may well account for the unexpectedly high resin preference for nitrate.

Coincidentally, the polymers with nitrogen in the matrix are also more polar (and hydrophilic) than polystyrene resins; the acrylic and aliphatic resins contain carbonyl groups while the epoxies and phenolics contain hydroxyl groups. In Diamond's view, large, poorly-hydrated, univalent anions tend to be rejected from an aqueous phase and have higher activity coefficients than predicted by the Debye-Huckel limiting law. His specific reasoning is that

"...Such ions intrude into the water structure without being able to orient the water molecules around themselves into coordinate hydration shells; as a result the water molecules nearest the ions are bound more tightly into the water structure beyond them".

Should the effect be considered applicable here it would help the systematic, resin phase preference for nitrate over chloride and the fact that nitrate is more preferred in more hydrophobic (polystyrene) resins. See Diamond [38] p. 257, for supporting arguments relating selectivity differences to the hydrophilic

and hydrophobic character respectively of cation vs anion-exchange resins (polystyrene-sulfonic acid vs. polystyrene-quaternary amine). Briefly, nitrate/chloride selectivities are ordered as follows:

polystyrene > non-polystyrene resins

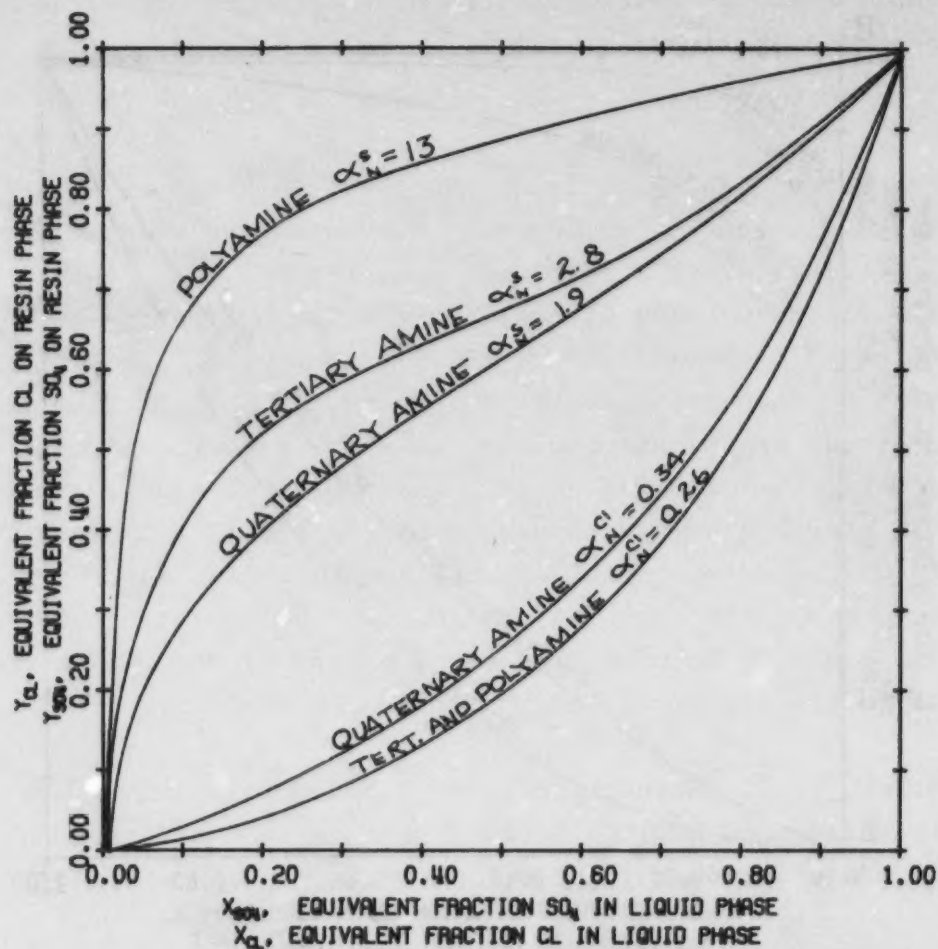
Functionality is nearly as important as nitrogen position in determining sulfate selectivity but has no apparent effect on the nitrate/chloride preferences of resins. See "Selectivity as Influenced by Functionality" for STY-DVB resins (Figure 22) and acrylic resins (Figure 23). Although the functionality effect on sulfate selectivity has previously been attributed to functional group basicity [13] no uniform correlation between basicity (pKa) and α_N^S was obtained here. Rather, the size and steric hindrance produced by the functional groups seem to be the determining factors; larger functional groups tend to prevent the required proximity of a pair of nitrogen atoms in addition to hindering the approach of the mobile counterions to the positively charged nitrogen centers.

Briefly, α_{Cl}^N is independent of functionality but α_S^N is greatly influenced by it. Nitrate/sulfate selectivities (α_S^N not α_N^S) are ordered as follows:

Quaternary > Tertiary >> Polyamine

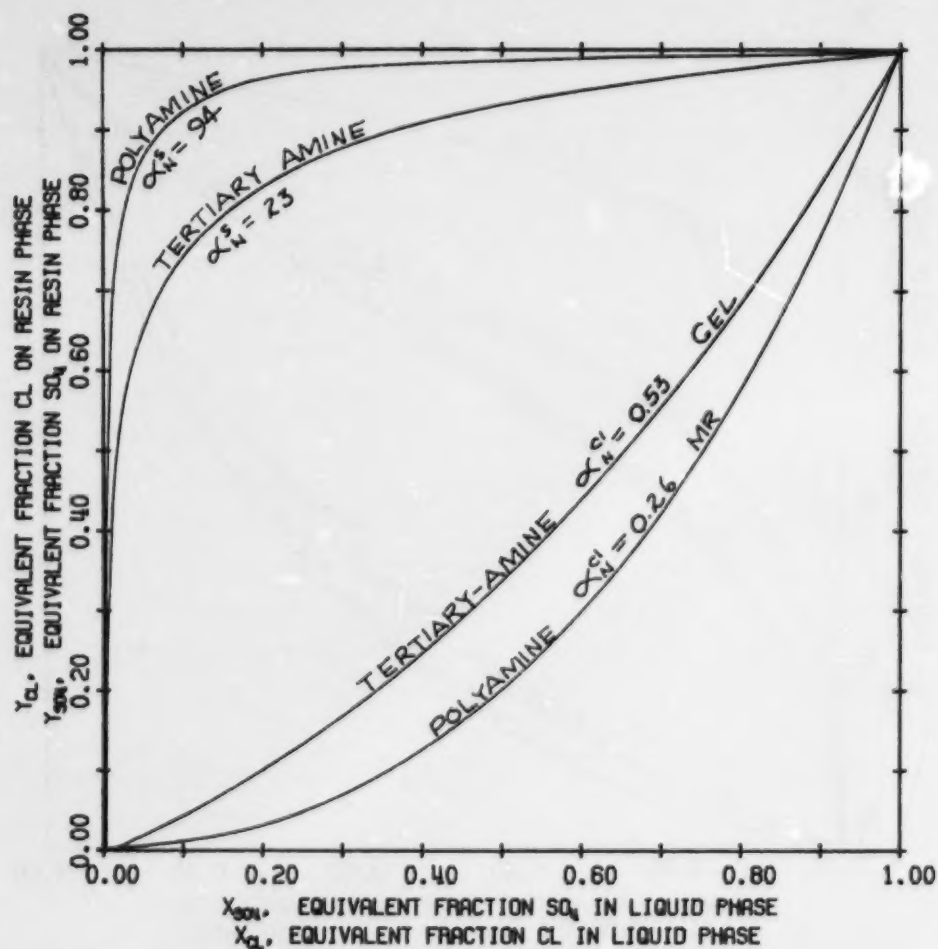
That is well demonstrated by Figures 22 and 23

Capacity is not a significant variable for predicting α_N^S or α_{Cl}^N even though high capacity (equated with high internal molality) should theoretically produce high sulfate selectivity. Capacity was mildly correlated with α_N^S for weak base resins but not for strong base resins. The presence of the capacity variable in the predictive equations doesn't add validity or



NO. 3; STYRENE-DVB, POLYAMINE RESIN, HCL CAP. = 1.76 MEQ./ML.
 NO. 8; STYRENE-DVB, TERTIARY-AMINE RESIN, HCL CAP. = 1.43 MEQ./ML.
 NO. 21; STYRENE-DVB, QUATERNARY-AMINE RESIN, HCL CAP. = 1.66 MEQ./ML.
 $C_I = 0.005$ N.
 $T = 25^\circ$ C

FIGURE 22
 SELECTIVITY AS INFLUENCED BY FUNCTIONALITY
 (ALL STYRENE-DVB MATRIX RESINS)



NO. 2; ACRYLIC-AMINE, TERTIARY-AMINE RESIN, HCL CAP. = 1.42 MEQ./ML.

NO. 10; ACRYLIC-AMINE, POLYAMINE RESIN, HCL CAP. = 2.59 MEQ./ML.

C₁ = 0.005 N.

T = 25° C

FIGURE 23
SELECTIVITY AS INFLUENCED BY FUNCTIONALITY
(ALL ACRYLIC-AMINE MATRIX RESINS)

reliability once the major effects due to matrix and functionality have been accounted for. See Selection of Regression in Appendix F.

Porosity is a major determinant of sulfate selectivity among Type I strong-base anion resins where isoporous resins with a relatively low degree of crosslinking are considerably more sulfate selective ($\alpha_N^S = 2.98$) than are the more-crosslinked gel and macroporous resins ($\alpha_N^S = 1.82$). Since hydration of the sulfate ion is not very significant (c.f. limiting ionic conductances Table 14) the screening by size due to higher degrees of crosslinking isn't expected to be significant. Greater flexibility of the polymer matrix permitting freer movement of the quaternary groups to pair-up with the divalent ion is offered as a possible explanation although the size-screening effect probably cannot be entirely ruled out. With this single exception of porosity being related to α_N^S for Type I SBA resins there are no significant effects of porosity on sulfate selectivity.

When porosity is converted to relative degree of crosslinking where:

isoporosity = 0.5

microporosity = 1.0

macroporosity = 2.0

the nitrate/chloride selectivity of non-polystyrene resins is found to be significantly increased when going from microporous to macroporous resins. If the increases in crosslinking are achieved by increasing the amine monomer to polar (i.e., epoxy, phenol, acrylic acid) monomer ratio, then macroporous (locally highly crosslinked) resins are more hydrophobic and would tend to favor the larger unhydrated-nitrate ion according to the explanation proposed by Diamond [38]. This is, in fact, the trend observed from the statistical analysis of the data. Furthermore, there is no significant correlation between relative

degree of crosslinking and nitrate/chloride selectivity for polystyrene resins. This is also as expected from the theory that nitrate selectivity is influenced by hydrophobicity which probably doesn't change as a result of increased crosslinking in STY-DVB resins. See Figures 20, 21, 10, and 11.

The basicity (pKa) of a resin doesn't appear to be a primary determinant of either sulfate/nitrate or nitrate/chloride selectivity although it is statistically and meaningful correlated with sulfate selectivity when non-polystyrene weak-base anion resins are considered. See Figure F6, Appendix. No new information is gained regarding either selectivity of any polystyrene resin except a Type II SBA resin from the knowledge of basicity after the most important independent variables, matrix and functionality, have been specified. Furthermore, the pKa's of weak-base resins (polystyrene and non-polystyrene) are unrelated to α_N^S or α_{Cl}^N . See Figures F4 and F5, Appendix.

Type II, strong base anion resins have higher sulfate selectivity ($\alpha_N^S = 2.99$) than do the Type I resins ($\alpha_N^S = 1.82$). Since the major difference here is basicity, one would be inclined to conclude that in this particular classification, i.e., Gel and macroporous, SBA resins, that reducing the basicity (pKa) increases the sulfate selectivity. However, for SBA resins as a group, porosity is as important as Type in determining selectivity, recall that the difference between isoporous ($\alpha_N^S = 2.98$) and MR or Gel ($\alpha_N^S = 1.82$) resins wrt sulfate selectivity was of almost exactly the same magnitude.

Predictive equations developed by the "selection of regression" technique, an optimization of the multiple regression analysis procedure, have verified that when considering all possible variables and all resins the most important determin-

ants of sulfate/nitrate selectivity are matrix and functionality while matrix and relative degree of crosslinking are the primary determinants of the magnitude of nitrate/chloride selectivity. Nevertheless, within particular subclasses of resins other factors such as type and basicity (pKa) do have significant further influences on α_N^S and α_{Cl}^N . All of these important relationships are summarized in the predictive equations and summary Tables 17 and 18 below. Note carefully, that in the tables, selectivities (separation factors) are given in α_N^S (not α_N^N) and α_{Cl}^N since it is the purpose there to summarize all of the influences on nitrate selectivity.

For Anion Resins in General: (Rough Estimate)

$$\alpha_N^S = \exp (2.3 \text{ N2POSITN} - 3.63 \text{ RSIZE} + 9.44) \quad (37)$$

$$\alpha_{Cl}^N = \exp (-0.371 \text{ N2POSITN} + 0.206 \text{ XLINKING} + 0.062) \quad (38)$$

For Weak-Base Anion Resins: (α_N^S , +10% at .005 N)
(α_{Cl}^N , +20%, independent of conc.)

$$\alpha_N^S = \exp (2.03 \text{ N2POSITN} - 7.45 \text{ RSIZE} + 17.44) \quad (39)$$

$$\alpha_{Cl}^N = \exp (-0.413 \text{ N2POSITN} + 0.381 \text{ XLINKING} + 0.755) \quad (40)$$

For Type I Gel and MR Strong-Base Anion Resins

$$\alpha_N^S = 1.82 \quad (\underline{+} 10\% \text{ at } .005 \text{ N}) \quad (41)$$

For all Type I, Isoporous, and Type II, Gel or MR, SBA Resins

$$\alpha_N^S = 2.98 \quad (\underline{+}10\% \text{ at } .005 \text{ N}) \quad (42)$$

For all strong base Anion Resins Regardless of Type or Porosity

$$\alpha_{Cl}^N = 3.14 \quad (+20\% \text{ independent of total conc.}) \quad (43)$$

Note: The N2POSITN dummy variable is indirectly related to the fundamentally important variable--distance of functional group separation. For polystyrene resins with pendant amine groups, containing one nitrogen atom this distance is expected to be randomly distributed, whereas it is controlled in polymers with the functional groups incorporated into the continuous structure by preselecting the amine monomers used in polymerization. Furthermore, it is conceivable to control the nitrogen separation distance and hence, the multivalent ion selectivity, in any new polymer, polystyrene or non-polystyrene.

α_N^S = Sulfate/nitrate separation factor

α_{Cl}^N = Nitrate/chloride separation factor

** N2POSITN = 1.0 for resins with nitrogen in the matrix (i.e., non-polystyrene resins)

** N2POSITN = 0.0 for resins with pendant nitrogen (i.e. polystyrene resins)

RSIZE = 2.0 for polyamine resins

RSIZE = 2.19 for tertiary amine resins

RSIZE = 2.36 for quaternary amine resins

XLINKING = 0.5 for isoporous resins

XLINKING = 1.0 for microporous resins

XLINKING = 2.0 for macroporous resins

TABLE 17

Variables Influencing Nitrate/Sulfate Selectivity α_S^N

++ = Greatly Increases α_S^N
 + = Increases α_S^N
 0 = No Significant Effect on α_S^N
 - = Decreases α_S^N
 -- = Greatly Decreases α_S^N
 N/A = Not applicable

	Anion Resins in General	Strong-Base Resins	Weak-Base Resins	Polystyrene Resins	Non-Polystyrene Weak-Base Resins	Type I Strong-Base Resins
	(1)	(2)	(3)	(4)	(5)	(6)
Nitrogen in Polymer Backbone	--	N/A	--	N/A	N/A	N/A
Increasing "R" Group Size	++	N/A	++	++	++	N/A
Increasing Degree of Crosslinking	0	+	0	0	0	+
Macroporous as Opposed to Microporous	0	0	0	0	0	0
Isoporous as Opposed to Gel or MR	N/A	-	N/A	N/A	N/A	--
Increasing Capacity	-	0	-	N/A	N/A	N/A
Type I as Opposed to Type II	N/A	+	N/A	N/A	N/A	N/A
Increasing pKa	+	0	0	0	++	N/A

Interpretation of Table:

Maximum Nitrate/Sulfate Selectivity is Associated with:

- (1) Polystyrene, quaternary, low capacity, anion resins
- (2) Non-isoporous, type I, strong-base anion resins
- (3) Polystyrene, tertiary, low capacity weak base anion resins

TABLE 18

Variables Influencing Nitrate/Chloride Selectivity α_{Cl}^N

++	=	Greatly increases α_{Cl}^N	Anion Resins in General (1)	Strong-Base Resins (2)	Weak-Base Resins (3)	Polystyrene Resins (4)	Non-Polystyrene Weak-Base Resins (5)	Type I Strong-Base Resins (6)
+	=	Increases α_{Cl}^N						
0	=	No Significant Effect on α_{Cl}^N						
-	=	Decreases α_{Cl}^N						
--	=	Greatly decreases α_{Cl}^N						
N/A	=	Not applicable						
Nitrogen in Polymer Backbone			--	N/A	--	N/A	N/A	N/A
Increasing "R" Group Size			0	N/A	0	-	0	N/A
Increasing Degree of Crosslinking			+	0	+	0	++	0
Macroporous as Opposed to Microporous			+	0	+	0	++	0
Isoporous as Opposed to Gel or MR			N/A	0	N/A	0	N/A	0
Increasing Capacity			0	0	0	0	0	0
Type I as Opposed to Type II			N/A	0	N/A	N/A	N/A	N/A
Increasing pKa			0	N/A	0	-	0	N/A

Interpretation of Table:

Maximum Nitrate/Chloride Selectivity is Associated with:

- (1) Polystyrene anion resins (Porosity and crosslinking aren't included because although they are relevant to anion resins in general, they are irrelevant to α_{Cl}^N for polystyrene resins)
- (3) Polystyrene Weak base resins
- (5) Macroporous (highly crosslinked) weak base anion resins

SECTION 6

PHASE II: MULTICOMPONENT CHROMATOGRAPHIC COLUMN STUDIES

OBJECTIVES

To determine if the separation factors (α_j^i) developed from binary equilibrium experiments can be used to predict the chromatographic behavior of the nitrate, sulfate, chloride and bicarbonate anions.

To determine whether or not differences exist in the quality of the effluent waters from the two types of processes, i.e., to compare single-bed, strong-base anions resin process performance to two-bed strong acid, weak-base process performance in chromatographic elution to nitrate breakthrough.

To determine the maximum possible chemical efficiencies and actual overall chemical efficiencies of various modifications of these two types of processes.

To determine if nitric acid and ammonium hydroxide can be used for cation and anion bed regeneration so that the wastewater, mostly ammonium nitrate, might be disposed of as a fertilizer.

To establish the comparative seriousness of the iron fouling problem in the single-bed and two-bed processes and to determine how it is influenced by the type of regenerant used.

To establish which of the thirty-two anion resins tested are best for nitrate removal service by determining which resin characteristics are most influential in maximizing the overall process efficiency.

PROCEDURAL OUTLINE

(1) Select resins for column studies based on α_N^S and α_{Cl}^N . Compare resins originally expected to be the best with low α_N^S and high α_{Cl}^N to worst resins, i.e., those with high α_N^S and low α_{Cl}^N .

(2) Establish bed depth and column diameters. One inch diameter (2.45) cm columns were specified as that was the minimum diameter guaranteed to be representative of large diameter columns. See Midkiff [86, p. 13], Dow Chemical Co. [4, p. 4], and The Duolite Manual [36, p. 26]. A bed depth of at least 24 in. (61 cm) was specified for the important comparison runs although a depth of 30 inches (76.2 cm) is usually recommended for one-inch diameter column studies [36, 41]. The justification here was that Midkiff [86, p. 76] found that nearly identical effluent profiles were obtained at bed depths beyond 22 inches [56 cm] even at flow rates up to 60 gpm/ft² (147 m/hr.) whereas the exhaustion flows used in these experiments were less than 5 gpm/ft² (12.2 m/hr.).

(3) Construct flow system. Representations of the entire experimental flow system are given in Figures 24 and D5 (Appendix) while column construction details are presented in Figures D6 and D7 (Appendix). The two-bed process flow schematic has already been discussed and its schematic flow diagram is Figure 1. For acid-elution experiments, the 2 1/2" dia. (6.35 cm) cation column containing 2.5 l of strong-acid cation resin preceded the weak-base anion bed (typically 0.31 l to insure that no cation breakthrough of Na⁺ salts occurred.

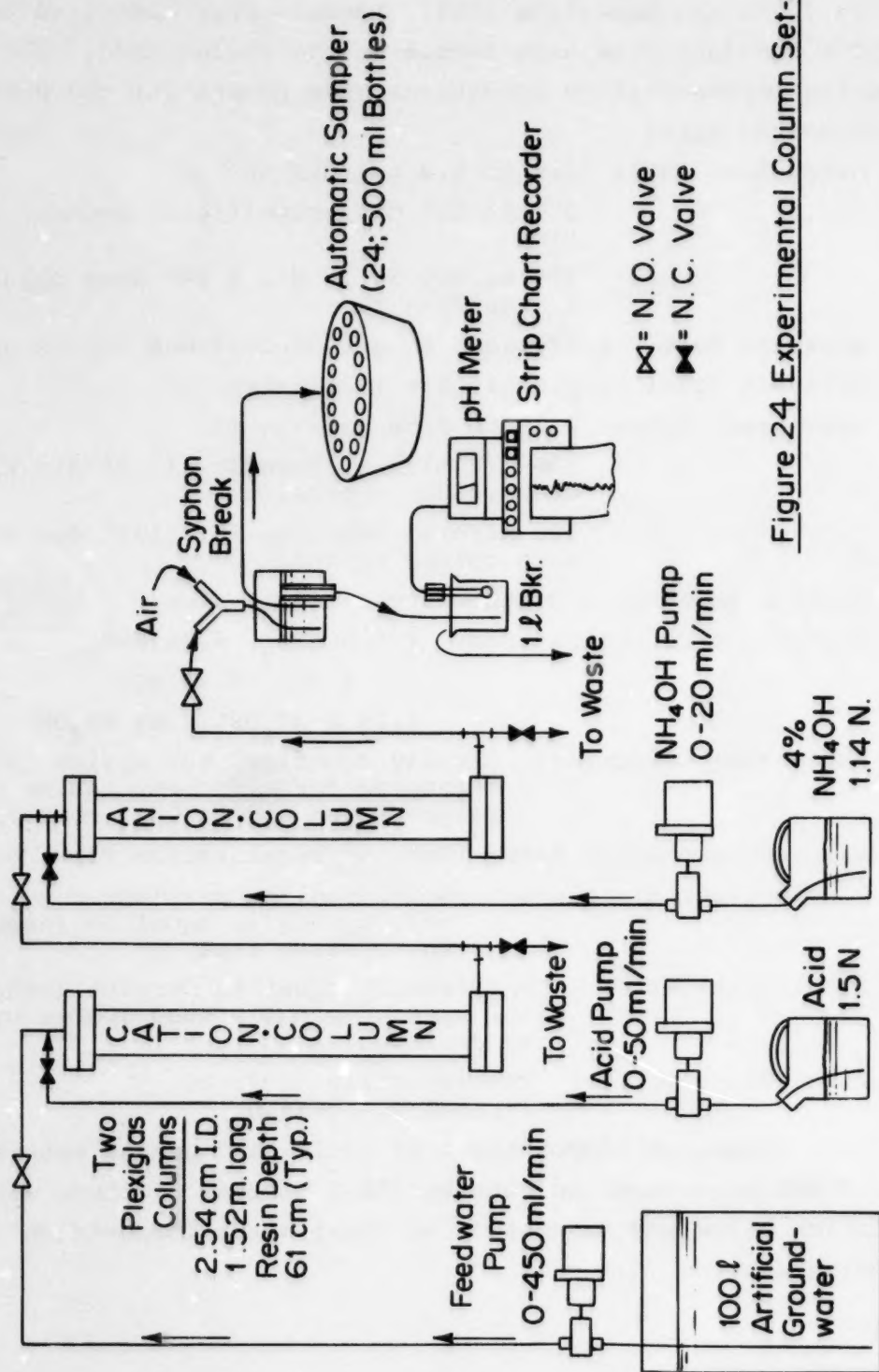


Figure 24 Experimental Column Set-up

(4) Choose range of operating conditions. The Dow [41], Duolite [37], and Amberlite [104] Manuals were consulted as were the manufacturers data sheets on the resins used. The following representative conditions were chosen for the experimental column runs:

Exhaustion Rate: 2.5 to 5.0 gal/min ft³
3.0 to 1.5 min. superficial detention time
103 ml/min in 1" dia x 24" deep column = 2.5 gal/min ft³

Backwash Rate: Sufficient to get 30-100% bed expansion

Backwash Time: Typically 5 - 10 minutes

Regenerant Rate: 0.25 to 0.50 gal/min ft³
10 - 20 ml/min, Downflow in 1" dia x 24" deep column typical
100 ml/min, downflow in 2 1/2" dia x 30" deep column typical

Minimum Regenerant Contact Time: 45 minutes

Regenerant Concentrations: 1.5 N HNO₃, 9.0% HNO₃
1.5 N HCl, 5.4% HCl
1.14 N NH₄OH, 4.0% NH₄OH

Regenerant Direction: Usually downflow, but upflow (HCl) attempted for efficient cation regeneration and Fe(OH)₃ removal

Displacement Rinse Rate: Same as regeneration flow rate

Displacement Rinse time: Sufficient to displace regenerant, typically equal to regenerant contact time.

Final Rinse Rate: Theoretically equal to service (exhaustion) rate, typically used 1/5 service rate overnight

Final Rinse Volume: Theoretically, 5-20 BV
Typically, 20-50 BV

(5) Establish compositions of artificial ground waters to be used and procedures to make up 100 l batches of these waters. See tables below and discussion on "Test Water Composition" in following section.

TABLE 19. TEST WATER 1 FOR RUN 1
Na TEST WATER FOR PRELIMINARY ACID ELUTION RUN*

X_i	Ion	meq/l	ppm
1.0	Na ⁺	5.0	115
.30	SO ₄ ⁼	1.5	72
.20	NO ₃ ⁻	1.0	62
.30	Cl	1.5	53
.20	HCO ₃ ⁻	<u>1.0</u>	<u>61</u>
Total Cations & Anions		5.0	363

$C_T = 0.005$ N = Total Concentration

NO₃-N = 14 ppm, $X_N = 0.20$

Note: For actual chemical composition of test waters, see
Appendix Tables D2 and D3.

* Acid elution of the anion bed means that acids not neutral salts were fed to the anion bed during the entire run, i.e., the H⁺ ion exchange capacity of the cation bed was greater than the OH⁻ ion-exchange capacity of the anion bed. Neutral elution means that neutral salts were fed to the anion bed during single-bed operation or that the H⁺ ion-exchange capacity was equal to or less than the OH⁻ ion-exchange capacity of the anion bed during two-bed operation.

TABLE 20. TEST WATER 2 FOR RUNS 2 THROUGH 8
Na TEST WATER FOR TWO-BED ACID ELUTION RUNS AND
SINGLE-BED NEUTRAL ELUTION RUN

X_i	Ion (i)	meq/l	ppm
1.0	Na^+	5.5	126.5
.27	$\text{SO}_4^{=}$	1.5	72.0
.27	NO_3^-	1.5	93.0
.27	Cl^-	1.5	53.2
.18	HCO_3^-	<u>1.0</u>	<u>61.0</u>
Total Cations & Anions		5.5	406

$C_T = 0.0055$ N = Total Concentration

$\text{NO}_3\text{-N} = 21$ ppm; $X_N = 0.27$

TABLE 21. TEST WATER 3 FOR RUNS 9 THROUGH 11
Ca-Mg-Fe TEST WATER FOR TWO-BED NEUTRAL ELUTION RUNS

	X_i	Ion	meq/l	ppm
Cations	.54	Ca^{++}	3.0	60
	.27	Mg^{++}	1.5	18
	.18	Na^+	1.0	23
	Nil	Fe^{++}	Nil	1
Anions	.27	$\text{SO}_4^{=}$	1.5	72
	.27	NO_3^-	1.5	93
	.27	Cl^-	1.5	53.2
	.18	HCO_3^-	<u>1.0</u>	<u>61</u>
Total Cations & Anions			5.5	381

$C_T = 0.0055$ N; $\text{NO}_3\text{-N} = 21$ ppm, $X_N = 0.27$

Hardness = 225 ppm as CaCO_3

Note: For actual chemical composition of test waters, see

Appendix Tables D2 and D3.

(6) Do preliminary test of system -- Run 1. This first run established that sharp effluent profiles could be produced in this flow system at 2.5 gal/min ft³ ($\tau = 3.0$ min) exhaustion rate with a bed depth of 25 inches (63.5 cm) and a total concentration of .005 N. Furthermore, a complete effluent profile could be produced in 1000 bed volumes (50 hours) with the resin of choice which at this point was Duolite ES-368 a MR, STY-DVB, tertiary amine resin with a capacity of 1.4 meq/ml and a particle size distribution favoring the smaller particles (30-40 mesh). See Column Effluent Profile, Run 1, Figure C1 (Appendix).

(7) Using acid elution to eliminate possible low-capacity effects, compare three, weak-base resins with very different selectivities. A flow rate of 5 gal/min ft³ ($\tau = 1.5$ min) was chosen to speed up the tests as the capacity of one resin chosen was 3.0 meq/ml, nearly double that of Run 1. This also offered the opportunity to determine the effect of exhaustion rate on efficiency. The following resins with wide ranging selectivities were chosen for these initial comparisons:

Resin	α_N^S	α_{Cl}^N
Duolite ES-368	2.83 (low)	3.87 (high)
Duolite ES-374	94.0 (high)	3.85 (high)
Dowex WGR	137 (high)	1.99 (low)

(8) Again, using acid elution to eliminate hydroxide ion interference, compare effluent profiles of resins with highly different sulfate selectivities but similar chloride selectivities at a relatively low flow rate: 2.5 gal/min ft³ ($\tau = 3.0$ min). Resins chosen were

Resin	α_N^S	α_{Cl}^N
Duolite ES-368	2.83 (low)	3.87 (high)
Duolite ES-374	94.0 (high)	3.85 (high)

(9) Establish the column performance of the single-bed strong-base anion system at the lower flow rate: 2.5 gal/min ft³ ($\tau = 3.0$ min). A macroreticular SBA resin from the least sulfate selective category was chosen for this run:

Resin	α_N^S	α_{Cl}^N
Ionac AFP 100	1.76	2.97

(10) Attempt a neutral elution of the two-bed system by balancing the cation and anion bed capacities by tailoring the regenerant level of the cation bed. Amberlite IRC-120 cation resin and Duolite ES-368 anion resin were utilized at the lower flow rate, 2.5 gal/min ft³. For these Runs (8, 9 and 10), the true, simulated Ca-Mg-Fe groundwater was used to exhaust the cation unit before it was regenerated at the level specified prior to being used in the two-bed run. The following regeneration levels based on the anion bed capacity were achieved for the cation bed which had a theoretically higher capacity (40% higher TEC) than the anion bed.

Run	Two-Bed Regeneration Level
8	600% of theory
9	120% of theory
10	240% of theory

See further discussion of "Regeneration Level" under Experimental Methods.

(11) Establish column performance of Amberlite IR-45 weak-base anion resin in two-bed neutral elution service at low flow (2.5 gal/min ft³) with Ca-Mg-Fe simulated groundwater. The two-bed performance of this moderately sulfate selective resin ($\alpha_N^S = 12.7$) in nitrate removal service has been reported in the literature [47] with some unusual results and so it was included for comparison purposes.

(12) Define ion-exchange process performance criteria on which to base judgements regarding the suitability or non-suitability of a given process or set of process operating conditions. The criteria selected were E_M and E_O where:

E_M = Maximum possible chemical efficiency in nitrate removal service.

E_O = Observed chemical efficiency in nitrate removal service.

See further discussion of "Definitions of Process Efficiency" under "Data Evaluation Methods".

(13) Establish acceptable breakthrough concentration of nitrate. See "Effluent Nitrate Breakthrough Concentration" following. The value chosen was 6.7 ppm (0.48 meq/l).

(14) Determine empirical efficiencies (E_M and E_O) of various runs by area measurement techniques on column effluent profiles and by observations of regeneration efficiency.

(15) Graphically compare throughputs (T) of various runs as measures of comparative process efficiencies.

(16) Establish comparative economics based on chemical regenerant costs, disposal costs and efficiencies (E_O).

(17) Rank the various processes and the anion resins as to their suitability for nitrate removal from ground waters having concentrations of ions similar to the representative Ca-Mg-Fe test water. Consider economics, organics bleed, possible iron fouling and regenerant waste water disposal.

(18) Calculate theoretical efficiencies (E_M and E_O) using the multicomponent chromatographic ion-exchange theory of Helfferich and Klein [63, 64] for test waters of similar and different compositions than those used in the column runs.

EXPERIMENTAL METHODS: (See also Appendix D)

The Criteria for Resin Selection

Of the weak base resins, the least sulfate selective were also the least chloride selective; these were all the STY-DVB, macroporous tertiary amine resins:

Resin	α_N^S	α_{Cl}^N
Amberlite IRA-93	3.75	4.86
Dowex MWA-1	2.67	4.43
Duolite ES-368	2.83	3.87
Ionac AFP-329	3.07	4.14

The further choice among these for a representative of what was expected would be the best column performance for a given class of resins was based on relatively minor differences wrt particle size distribution and organics bleed as measured by UV adsorption. Having considered all these variables, Duolite ES-368 was chosen primarily because of its finer, more consistently sized particles. It did however have, as did all but Ionac AFP-329, significant organics bleed as indicated by UV adsorbance. Furthermore about 10% of the beads had a tendency to float during backwash, a possible problem which would have to be considered seriously in any large-scale installation.

Effluent NO₃ Breakthrough Concentration

In a bypass blending system such as the one proposed (Fig. 1), the question arises as to what range of nitrate concentrations is acceptable in the blended effluent and what factor of safety is appropriate. The legal limit is 10 ppm NO₃-N and, an appropriate blended NO₃-N concentration might be one-half that value. Assuming an influent concentration of 20 ppm NO₃-N to the ion-exchange process the flow split would be:

$$\begin{aligned}\text{Feed} &= Q \\ \text{Flow to Columns} &= .75Q \\ \text{Bypass Flow} &= .25Q\end{aligned}$$

With such a split, one would have to limit the $\text{NO}_3\text{-N}$ breakthrough concentration to 6.7 ppm (0.48 meq/l) so as not to exceed the 10 ppm allowable maximum in the blended water. The appearance of that effluent concentration then determines the end of a run. Clearly the economic efficiency of the process is inversely proportional to the safety factor chosen. For example, allowing 8 ppm $\text{NO}_3\text{-N}$ in the blended water would permit 40%, as compared to 25% of the influent flow to be bypassed. However this leads to a maximum allowable breakthrough concentration of 3.3 ppm (0.24 meq/l) which would necessitate earlier termination of the run. But, from the experimental data, the loss in bed volumes treated to 3.3 ppm $\text{NO}_3\text{-N}$ breakthrough compared to 6.7 ppm $\text{NO}_3\text{-N}$ would be only about 10% which is more than offset by the 60% gain in permissible, bypass flow (40% bypass compared to 25%). Nevertheless, operation to such a low breakthrough concentration is not recommended since some preliminary leakage of nitrate might be expected as was evidenced in Run 10 (Fig. C10) where a preliminary $\text{NO}_3\text{-N}$ plateau reached a level of 0.24 meq/l and would have necessitated premature termination of the run.

For the reasons stated above, the evaluations of process efficiency and economics in this work based on:

- 21 ppm (1.5 meq/l) $\text{NO}_3\text{-N}$ in Ground Water
- 25% bypass of Raw Water
- 5 ppm $\text{NO}_3\text{-N}$ in Blended Effluent
- 6.7 ppm $\text{NO}_3\text{-N}$ breakthrough $\text{NO}_3\text{-N}$ concentration

Level of Regeneration in Two-Bed System

Weak-base resins are so selective for hydroxide ions that they are nearly stoichiometrically regenerated (110% of theory) even with weak bases like NH_4OH . This advantage is lost however, when a weak-base resin follows a strong-acid cation bed as it must in the treatment of nearly neutral to basic water supplies. The reasoning has to do with the required neutralization of regenerant wastewaters: a requirement which dictates that there be as much excess base as acid. Since regeneration of the strong-acid cation bed is quite inefficient (300% of theory) especially in divalent calcium and magnesium ion removal service, the NH_4OH saved during efficient, anion-bed regeneration must be expended to neutralize the inevitable excess acid from strong-acid cation regeneration. This does not negate the basic reason for choosing a weak-base anion resin to solve the regenerant disposal problems, i.e., to allow a weak base like NH_3 to be the regenerant thereby eliminating the agriculturally undesirable cations, Na^+ and K^+ from the regenerant wastewaters and providing instead the agriculturally desirable NH_4^+ cation.

Because of this unavoidable disparity in cation and anion bed regeneration efficiencies, a regenerant design procedure based on the capacity of the anion unit was utilized. Once the exchange capacity of the anion bed was specified, an amount of cation resin was provided which had a total equivalent capacity (TEC) at least 20% greater than that of the anion bed. The level of regeneration specified was then expressed in terms of per cent of theoretical anion bed capacity. That regeneration level was applied to both beds assuming they were of equal (anion bed) capacity. A very large excess of regenerant cannot be applied indiscriminantly because once the capacity of the anion bed is utilized completely by the strong acids: HCl , HNO_3 and H_2SO_4 , its effluent will then be very acidic ($\text{pH} = 2.4$

for these 0.005 N test waters) and that condition will always occur before nitrate breakthrough as chloride is always the first strong-acid anion to appear in the effluent. On the other hand, if insufficient acid regenerant is applied, the cation bed will be exhausted before the strong acid capacity of the anion bed is utilized. This results in a neutral influent to the anion bed and a much reduced anion bed capacity in addition to a probable change in the separation factors among all the ions of interest; both of these changes substantially increase the difficulty of predicting the breakthrough profiles. The difficulty of efficiently balancing the acid and base regenerants is admittedly a disadvantage with any two bed ion-exchange process, nevertheless it is not overly difficult and once solved for a given installation should remain solved as long as the composition of the ground water and the capacities of the resins remain relatively constant.

Sample Collection During Column Runs

Automatic sampling from the one liter overflow vessel (Fig. 24) was accomplished using a Manning Wastewater Sampler; samples were usually taken once/hr except during Run 6 when the rate was once/2hr. Typical length of a run was 48 hours except for Run 6 which lasted 100 hours. Flow rates were either 20 BV/hr (Runs 1 & 5-11) or 40 BV/hr (Runs 2-4) and of such duration as to give 800-2000 BV of cumulative total flow.

Carbonic Acid & Bicarbonate Analyses During Runs

Because H_2CO_3 and HCO_3^- weren't removed to any appreciable extent by the anion resins, they appeared quite early in the effluent profiles. For all the two-bed runs, H_2CO_3 was the dominant species (effluent pH 2.3 -- 4.6) and was easily lost upon exposure to the atmosphere. To eliminate the loss due to CO_2 volatilization, hourly, manual samples were taken directly

from the flowing effluent stream by syringe and immediately injected into the inorganic channel of the Beckman TOC analyzer for CO_2 analysis. Once the H_2CO_3 effluent profile had been established, hourly samples were stopped and only an occasional sample was taken. All H_2CO_3 and HCO_3^- analysis were accomplished in this manner irrespective of the effluent pH.

DATA EVALUATION METHODS: DEFINITIONS AND MEASUREMENTS OF PROCESS EFFICIENCIES

Maximum Possible Chemical Efficiency

Maximum possible chemical efficiency (E_M) is defined simply as $\bar{y}_N$ the average equivalent fraction of nitrate on the resin at the end of the run. Since y_N varies with distance into the bed, the weighted average value $\bar{y}_N$, must be used to represent the ratio of nitrate removed to all ions removed. In the ideally efficient process this would of course approach 1.0 which would only be possible if nitrate were much preferred over all other anions which it is not in these experiments.

$$E_M = \bar{y}_N = \frac{\text{meq NO}_3^- \text{ on resin at end of run}}{\text{Total meq of ions on resin at end of run}} \quad (44)$$

$$\bar{y}_N = \frac{\text{meq NO}_3^- \text{ in} - \text{meq NO}_3^- \text{ out}}{\text{Initial meq of all ions} + \text{meq of all ions in} - \text{meq of all ions out}} \quad (45)$$

$$\bar{y}_1 = \bar{y}_N = \frac{C_{1,0}V_e - \int_0^{V_e} C_1 dV}{\sum_{i=1}^4 \left[V_e C_{i,0} - \int_0^{V_e} C_i dV \right]} \quad (46)$$

where subscripts: 1 = NO_3^- , 2 = SO_4^{--} , 3 = Cl^- , 4 = HCO_3^- and $C_{i,0}$ = influent (initial) phase conc. of component i and all other symbols are as defined in the nomenclature. Run 7 is a special case as regards determination of E_M since the resin was initially saturated with the exchanging counterion, Cl^- , which,

upon exchange, was accounted for in the effluent. This is contrasted to all the other runs where the resins were initially in the free base (FB) form and no measureable counterions were released upon acid adsorption (or, alternatively, upon ion-exchange where OH^- was considered the counterion which was neutralized upon exchange). For Run 7 then:

$$\bar{y}_1 = \bar{y}_N = \frac{C_{1,0}V_e - \int_0^{V_e} C_1 dv}{Q_{Cl}v + \sum_{i=1}^4 \left[V_e C_{i,0} - \int_0^{V_e} C_i dv \right]} \quad (47)$$

where $Q_{Cl}v$ = chloride capacity of bed = $\frac{\text{meq}}{\text{ml}} * \text{ml}$. Example calculations of efficiencies (E_M) for Runs 7 & 11 are given in Appendix E.

Overall Chemical Efficiency

Overall chemical efficiency (E_C) is product of the maximum possible chemical efficiency (E_M) and the observed regeneration efficiency (E_R).

$$E_O = E_M E_R \quad (48)$$

$$E_R = \text{Regeneration Efficiency} = \frac{\text{meq total capacity of anion bed}}{\text{meq anion regenerant applied}} \quad (49)$$

$$E_O = \text{Overall Chemical Efficiency} = \frac{\text{meq NO}_3^- \text{ removed}}{\text{meq anion regenerant applied}} \quad (50)$$

Ordinarily E_R is near 0.9 because of the ease with which weak base resins are regenerated but, as has been pointed out in the "Level of Regeneration" discussion, the need to neutralize the excess cation regenerant greatly reduces the overall regeneration efficiency.

Summarily, the lion's share of ion-exchange operating costs

will be for regenerant chemicals and possibly for their disposal. Each equivalent of nitrate removed from the water supply will require $1/E_0$ equivalents of anion and, if applicable, cation-regenerant chemicals. Three procedures were studied here to improve the overall efficiencies of these processes:

- (1) selection of resins with low α_N^S and high α_{Cl}^N .
- (2) chromatographic elution of the lesser preferred ions, HCO_3^- and Cl^- , to increase $\bar{y}_N$, the average equivalent fraction of nitrate on the resin at the end of a run and
- (3) minimization of the excess regenerant utilized.

The maximum possible chemical efficiency, E_M , is very much dependent on the ionic composition of the water to be treated over which no control can be exerted in actual practice. With Test Water 1, Table 19, for example, $x_S = 0.3$, $x_N = 0.2$ and $E_M = 0.4$ if no chloride or bicarbonate are removed while all sulfate and nitrate are removed. Slightly better efficiency is possible with Test Water 2 Table 20 where $x_S = .27$, $x_N = 0.27$ and $E_M = 0.5$ if all the nitrate and sulfate and none of the bicarbonate and chloride are removed. Even though these efficiencies are moderately low, they would be much lower in conventional deionization or ion-exchange service where the run would terminate on conductivity breakthrough or when the theoretical capacity of the anion bed was exhausted. In these instances chloride and possibly bicarbonate would still occupy a significant portion of the exchange sites and E_M for Test Water 1 could be as low as 0.2 or as low as 0.27 for Test Water 2. Generally the maximum possible chemical efficiency (E_M) has x_N , the liquid phase equivalent fraction of nitrate, as its lower limit corresponding to the complete deionization case without any chromatographic elution.

VISUAL INTERPRETATION OF COLUMN EFFLUENT PROFILES

Plateaus and Plateau Concentrations

The effluent concentration vs bed volumes of effluent curves for all eleven runs are plotted in Figures C1-C13 (appendix C). Consider RUN 1 as typical of the general effluent behavior of the four anions of interest and note that, as predicted, there are four plateaus each corresponding to one of the anions, and that these plateaus are separated by rather abrupt transition zones. The first component to appear is always H_2CO_3 or HCO_3^- followed by Cl^- , NO_3^- and finally $\text{SO}_4^{=}$ the most preferred species. Observe also that, as expected, all species save for the most preferred $\text{SO}_4^{=}$ appear at some time in the effluent in concentrations from 20 to 300% higher than in the feed water (C_0). Abrupt increases in concentration of one component are always accompanied by a correspondingly abrupt concentration decrease in a second component once the H_2CO_3 has been eluted and true ion-exchange is maintaining the total, liquid, effluent concentration at approximately that of the influent concentration: 0.005 N for RUN 1 and .0055 N for all others.

Nitrate Breakthrough Profiles

In all the low flow rate runs ($2.5 \text{ gal/min} \cdot \text{ft}^3$), the nitrate breakthrough curves are quite sharp but not vertical meaning that the end of the run is rather abrupt but not without warning - a desirable feature for a full-scale, nitrate removal installation. It is also consistently observed that some preliminary, though minor, breakthrough of nitrate occurred with Duolite ES-368; see Runs 1, 5, 8, 9, and 10, all at 2.5 gal/min ft^3 . The problem is at its worst in Run 9 where the influent became neutral prematurely due to incomplete regeneration of the cation bed (120% of theory) and nonexistent under

the high flow rate (5 gal/min ft³) acid elution conditions of Run 3.

Recall that the nitrate breakthrough concentration has been conservatively chosen as 0.48 meq/l (6.7 ppm NO₃-N) and that the effluent volume at that point is labelled V_e indicating the end of the run for nitrate removal service.

DISCUSSION OF COLUMN RUN RESULTS

Phase II Data Summary: Column Performance Characteristics

The important results from the column runs are listed in Table 22 below. Five different resins with sulfate/nitrate selectivities varying in the range of 2.83 to 137 and having nitrate/chloride selectivities in the range of 1.99 - 3.87 were evaluated at two different superficial detention times: 2.44 gal/min ft³ in 61 cm deep beds ($\tau = 3.1$ min) and 4.88 gal/min ft³ in 30.5 cm deep beds ($\tau = 1.5$ min). Runs 1-6 were acid elution experiments where the cation bed was much larger than the anion bed to insure constant capacity and provide ideal conditions for the prediction of efficiency and the determination of the effects due to varying α_N^S and α_{Cl}^N . Run 7 was a single strong-base anion column run for the purpose of comparing the performance of this currently used NaCl-regeneration process to the proposed two-bed system. Runs 9-11 were neutral elution runs with a Ca-Mg-Fe containing groundwater under conditions which simulated as closely as possible those expected in a full-scale, nitrate removal installation on groundwater.

Factors Influencing E_M: Maximum Possible Chemical Efficiency

Range of Variation of E_M ($\bar{y}_N$)

There is a surprisingly narrow range of efficiencies

TABLE 22: COLUMN PERFORMANCE CHARACTERISTICS

Run No.	* Flow $\frac{\text{gal}}{\text{min. ft}^3}$	Minimum pH Final ph	Bed Depth cm	Resin Description (Cation Regeneration Level)	S _N	N _{Cl}	Y _{Cl}	Y _S	Y _{HCO₃}	Y _N	** Final Column Capacity meq/ml	+ Ve BV
1	2.34	2.5 2.5	63.5	Duolite ES-368 STY-DVB, Tert-Amine, MR	2.83	3.87	.13	.53	.00	.34	1.65	582
2	4.88	2.5 2.5	30.5	Duolite ES-374 Polyacrylic, Polyamine, MR	94.	3.85	.26	.36	.02	.36	2.93	720
3	4.88	2.4 2.4	30.5	Duolite ES-368 STY-DVB, Tert. Amine, MR	2.83	3.87	.20	.40	.01	.39	1.36	364
4	4.88	2.5 2.5	30.5	Dowex WGR Epoxy-Amine, Polyamine, Gel	137.	1.99	.27	.37	.00	.36	1.62	391
5	2.44	2.4 2.4	61.0	Duolite ES-368 STY-DVB, Tert. Amine, MR	2.83	3.87	.16	.43	.00	.41	1.48	423
6	2.44	2.3 2.5	61.0	Duolite ES-374 Polyacrylic, Polyamine, MR	94.	3.85	.15	.44	.00	.41	3.12	920
7	2.44	6.1 7.4	61.0	Ionac AFP-100 STY-DVB, Quat. (1)Amine, MR	1.76	2.97	.14	.43	.01	.42	1.03	295
8	2.88	2.8 5.8	61.0	Duolite ES-368 (600%) STY-DVB, Tert. Amine, MR	2.83	3.87	.21	.40	.00	.39	1.39	375
9	2.44	4.5 6.7	61.0	Duolite ES-368 (120%) STY-DVB, Tert. Amine, MR	2.83	3.87	.31	.34	.02	.33	0.84	190
10	2.44	4.6 6.3	61.0	Duolite ES-368 (240%) STY-DVB, Tert. Amine, MR	2.83	3.87	.14	.44	.00	.42	1.15	334
11	2.44	4.7 5.5	61.0	Amberlite IR-45 (300%) STY-DVB, Polyamine, Gel	12.7	3.89	.08	.45	.03	.44	1.61	480

* $\frac{\text{gal}}{\text{min. ft}^3} \times 7.48$ = Superficial detention time, τ , minutes+ Ve = Bed volumes of effluent to 0.5 meq/l NO₃-breakthrough (end of run)

** Final Column Capacity is greater than measured HCl capacity because resin has higher capacity for sulfate which occupies a significant fraction of the available sites at the end of the run.

Final pH refers to the pH of the system effluent at nitrate breakthrough.

Minimum pH was the minimum pH observed during the course of the run.

($E_M = \bar{y}_N$) among all the runs where valid comparisons might be made. It is not intuitively obvious that such small variations in the nitrate content of the spent resins should result from such large differences in α_N^S . However, as it turns out, α_{Cl}^N is more important in determining $\bar{y}_N$ than is α_N^S , and with a much smaller range of values existing for α_{Cl}^N the narrow range is not surprising after all.

Breakthrough Volume (V_e) and Bed Capacity (meq/ml)

Here is where the largest variations are found among the resins. Simplified theoretical considerations dictate that capacity shouldn't influence the chemical efficiency of these processes because the important factor is E_M where:

$$E_M = \frac{\text{meq nitrate on resin at end of run}}{\text{Total meq of ions on resin at end of run}} \quad (44)$$

which is independent of capacity per se. However, the practical considerations of bed size required and rinse volume required definitely favor the high capacity resins which permit smaller resin beds and less rinse volumes to be used. An exception to this has been reported (D. Harrington, Dow Chemical Co., personal communication) for highly sulfate selective resins (especially epoxy-amine resins) which require increasingly larger rinse volumes with time, an effect reportedly occurring only in waters where sulfate represents a large fraction of the total anions present.

Nitrate Selectivity vs. Column Efficiency (E_M or $\bar{y}_N$)

The effects of both α_N^S and α_{Cl}^N can be determined by comparing runs in which these were the only variables; c.f. Runs 2, 3, and 4; Runs 5 & 6; Runs 7, 10 & 11. Direct comparisons among these runs are provided in the throughput graphs (Figs. 25 - 27) and by comparing efficiencies (E_M or $\bar{y}_N$) in Table 22 for these groups of resins. Runs 2, 3, and 4 yielded the most non-ideal effluent profiles and the lowest efficiencies for nitrate: 0.36, 0.39 and 0.36 respectively. The greatest

portion of the differences in these efficiencies is attributed to kinetic not thermodynamic considerations. The average equivalent fractions of chloride on the resins were highest for this flow condition ($4.88 \text{ gal/min} \cdot \text{ft}^3$); the short columns (30.5 cm) and detention times ($\tau = 1.53 \text{ min}$) apparently promoted chloride removal beyond that expected due to equilibrium separation. Duolite ES-368 with low α_N^S and high α_{Cl}^N did provide the highest efficiency (Run 3, $E_M = .39$) but the trend of the data among the runs was not consistent. Dowex WGR was expected to be the worst due to its high α_N^S and low α_{Cl}^N but it performed equally as well as Duolite ES-374 with high α_N^S and high α_{Cl}^N . See Figure 25. Again, these obviously non-ideal results with Runs 2, 3, and 4 are attributed to the short columns and short detention times.

The nitrate effluent breakthrough profiles of Runs 5 and 6 (Fig. 27) are nearly identical which was, at first, surprising for resins with such different sulfate selectivities: $\alpha_N^S = 2.83$ for Run 5 and $\alpha_N^S = 94$ for Run 6. However, the nitrate/chloride selectivities of these resins are nearly identical ($\alpha_{Cl}^N = 3.85$) and that apparently is the separation factor which determines the nitrate breakthrough and efficiency $\bar{y}_N$.

The same sort of situation exists for Runs 7, 10 and 11 (Fig. 26) where α_N^S varies from 1.76 to 12.7 while α_{Cl}^N only varies from 2.97 to 3.87. Again, the nitrate breakthrough profiles are nearly superimposable and the maximum possible chemical efficiencies for nitrate removal are nearly identical: 0.42, 0.42 and 0.44 for Runs 7, 10 and 11 respectively.

Briefly, the experimental data from those runs where the approach to equilibrium was close indicated that it is the nitrate/chloride selectivity not the sulfate/nitrate selectivity which primarily determined the average equivalent fraction of nitrate on the resin at the end of an ion-exchange column run

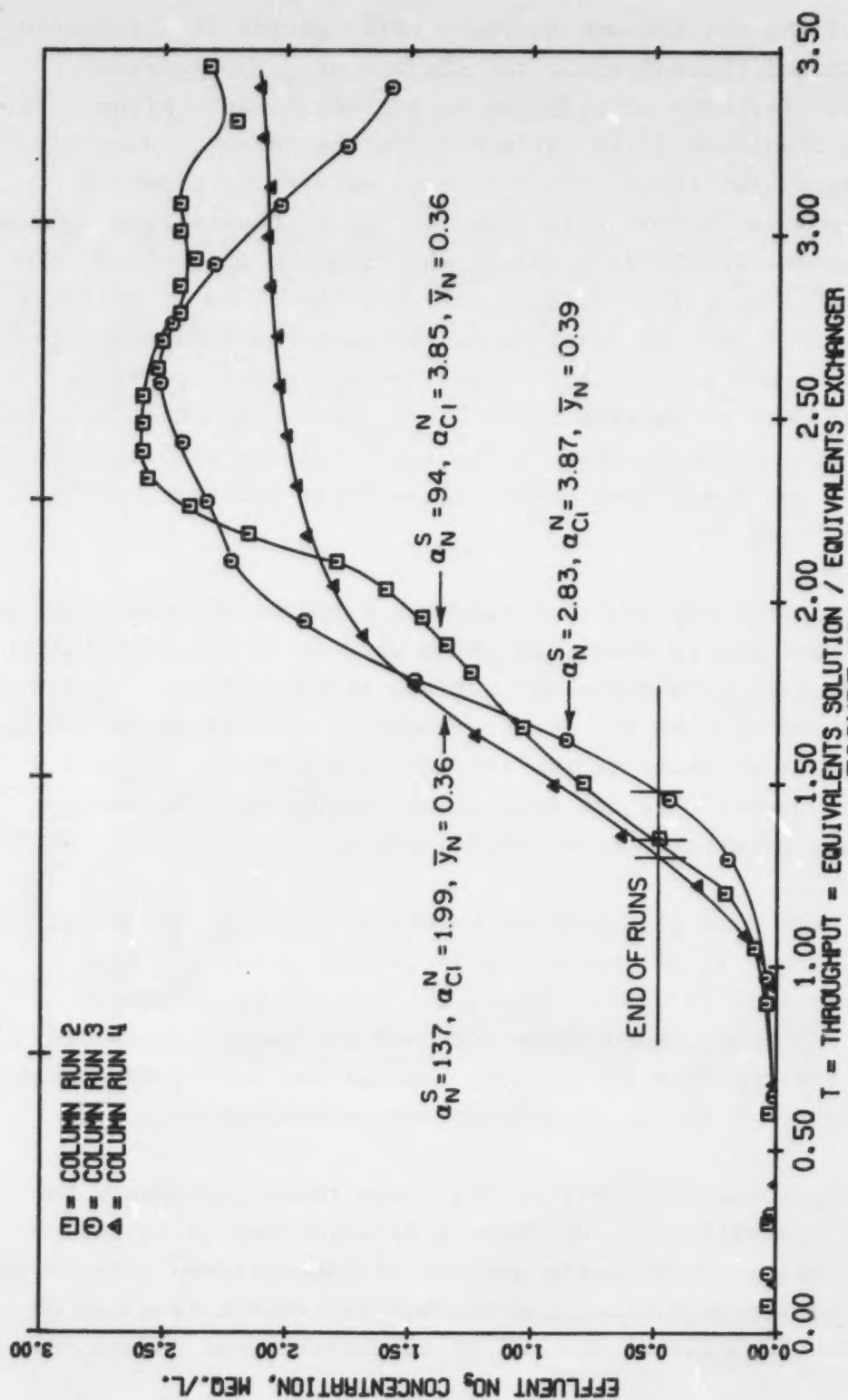


FIGURE 25
 COLUMN EFFLUENT PROFILES (NITRATE)
 EFFECT OF SULFATE AND CHLORIDE SELECTIVITIES ON COLUMN EFFICIENCY

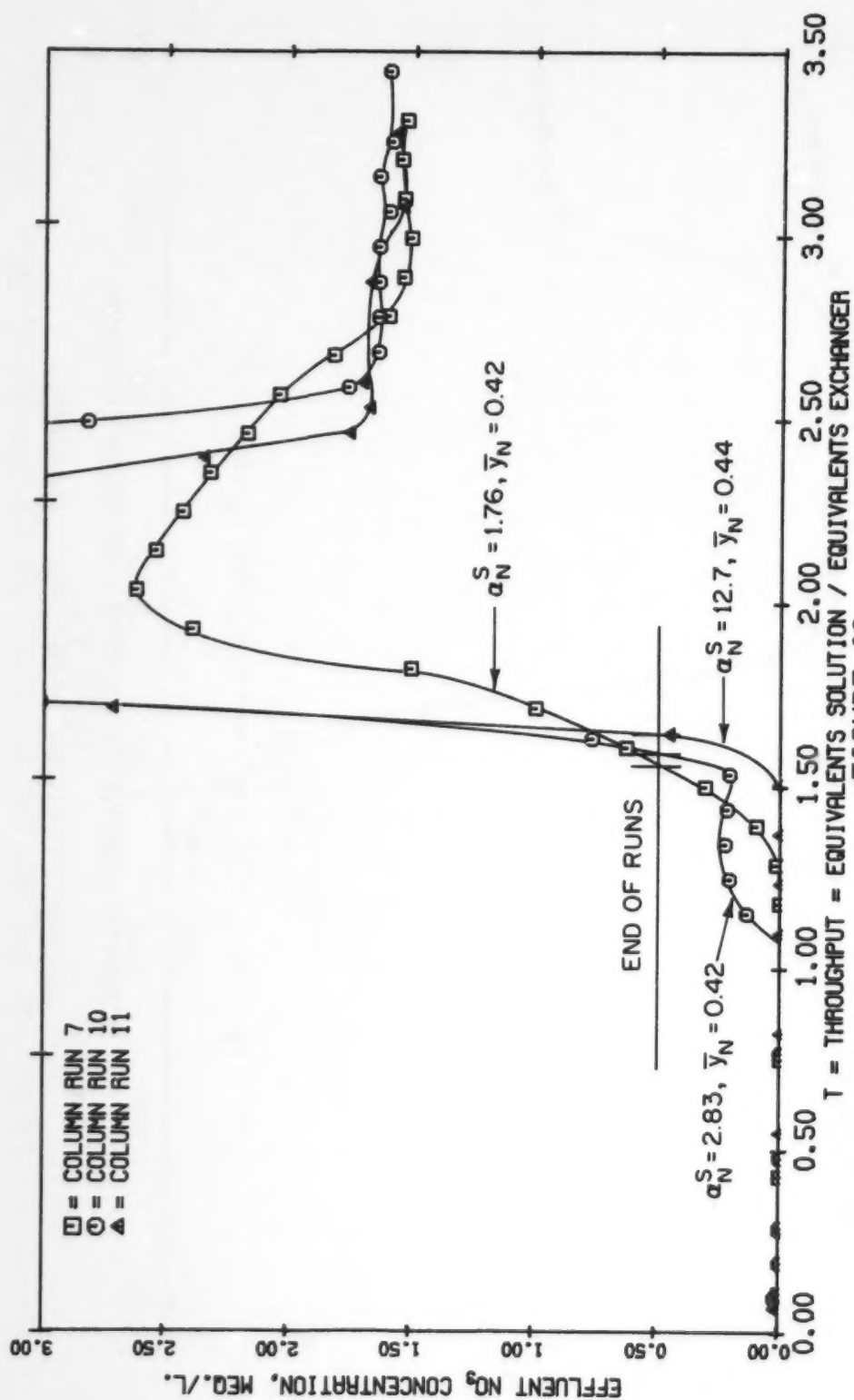


FIGURE 26
COLUMN EFFLUENT PROFILES (NITRATE)
EFFECT OF SULFATE SELECTIVITY ON COLUMN EFFICIENCY

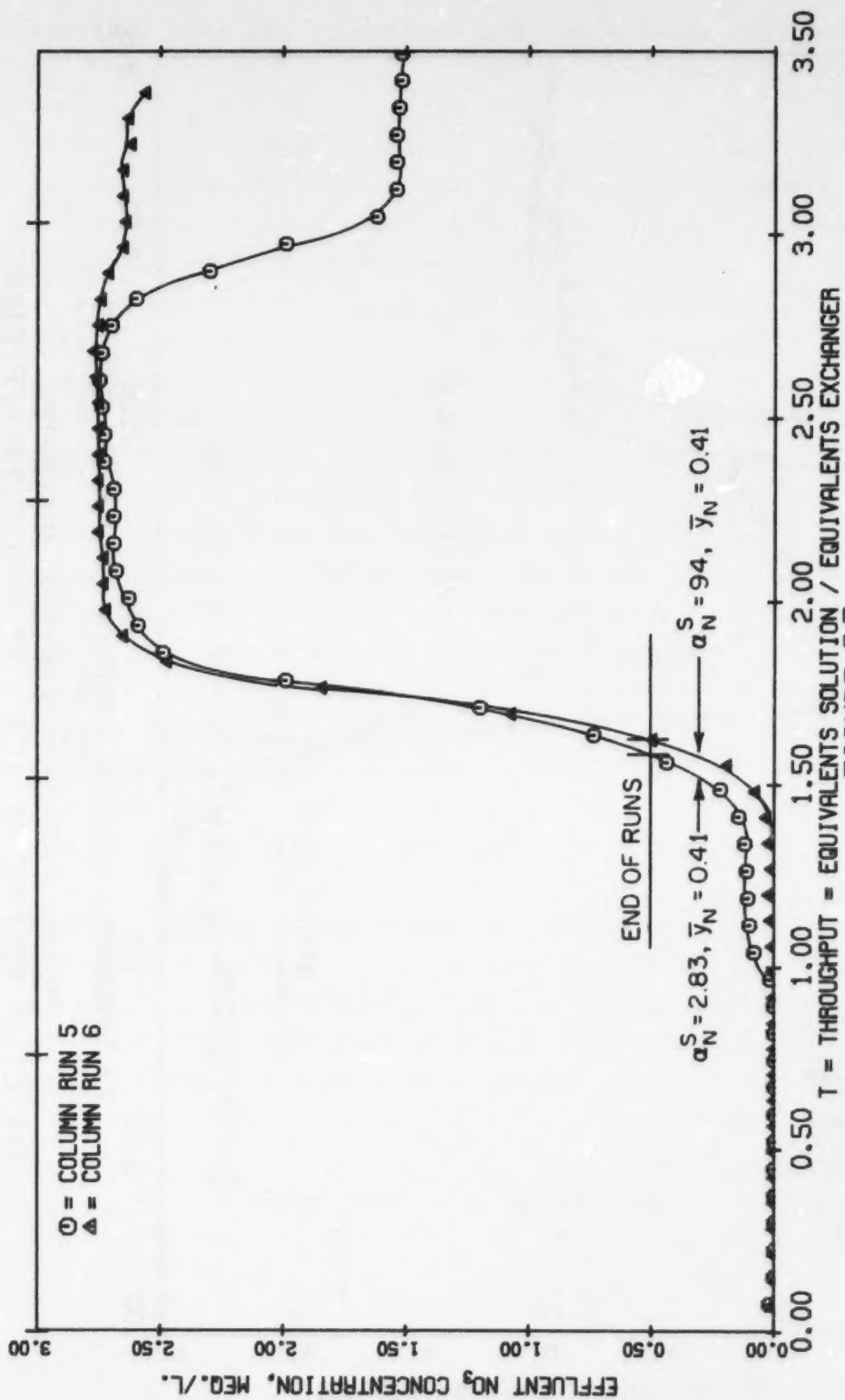


FIGURE 27
 COLUMN EFFLUENT PROFILES (NITRATE)
 EFFECT OF SULFATE SELECTIVITY ON COLUMN EFFICIENCY

terminated upon chromatographic elution of the ions less preferred than nitrate.

Exhaustion Rate, Bed Depth and Detention Time

Only one actual flow rate (103 ml/min) was employed in all the runs. This corresponded to 20 BV/hr or 2.44 gal/min ft³ in the deep, 24 in. (60.5 cm) beds and to 40 BV/hr or 4.88 gal/min ft³ in the shallow beds - 12 in. (30.5 cm). Very significant differences resulted from varying the bed depth. See especially Runs 2 and 4 (Figs. 25, C2 and C4) and note the non-ideal effluent profiles. Both these Runs were made with the kinetically slower microporous resins compared to Run 3 made at the same bed depth but with a macroporous resin. Compare Runs 2 and 6 (Fig. 28) and note the drastic change in sharpness and ideality of the effluent profiles which was produced with this high capacity, microporous resin as a result of increasing bed depth from 12 to 24 inches with a corresponding increase in actual detention time from 0.75 to 1.5 minutes (assuming a bed porosity of 0.5). These short fluid detention times are misleading; the real effect is the doubling of the length of the run from 50 to 100 hours thereby allowing much more time for most of the bed to come to equilibrium.

For the development of reasonably ideal effluent profiles, an exhaustion rate of 2.5 gal/min ft³ or less is recommended. Rates higher than this reduce the chemical efficiency, $\bar{y}_N$, in nitrate removal service by allowing much more chloride to remain in the bed; c.f. the $\bar{y}_N$ values between Runs 2 and 6 and between Runs 3 and 5 below:

Run	gal/min ft ³	cm Bed Depth	$\bar{y}_N$
2	4.88	30.5	.36
6	2.44	61.0	.41
3	4.88	30.5	.39
5	2.44	61.0	.41

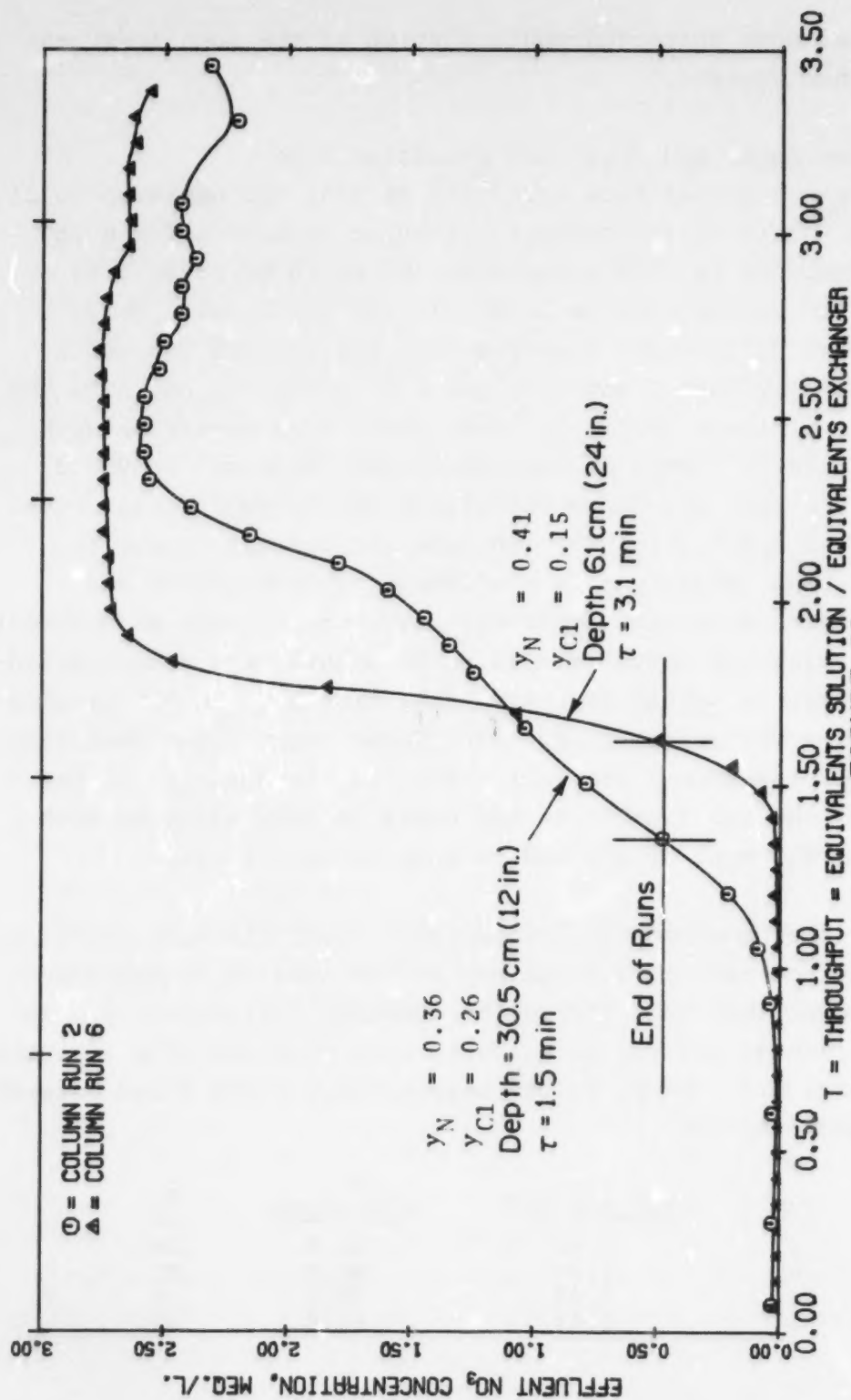


FIGURE 28

COLUMN EFFLUENT PROFILES (NITRATE)
EFFECT OF BED DEPTH AND DETENTION TIME ON COLUMN EFFICIENCY

These changes due to exhaustion rate (bed depth) might not seem large but they are larger than those produced by the selectivity differences of the commercial anion resins used in these experiments.

Regeneration Level vs. Efficiency (E_M): Runs 8-11

A significant reduced column capacity and efficiency ($\bar{y}_N = 0.33$) resulted from the low regeneration level (120% of theory) of Run 9. Note also the unusual nitrate profile with a significant premature nitrate peak which forced termination of the run at 190 BV. The final capacity was only 0.84 meq/ml compared to 1.48 meq/ml for the acid elution run (Run 5) and 1.15 meq/ml for the successful neutral elution run (Run 10).

Run 8 represented an unsuccessful attempt at neutral elution: regeneration level = 600% of theory for Duolite ES-368. The cation bed consequently had too much capacity and didn't break through soon enough. Thus, the effluent pH from the system dropped to 2.8, an unacceptable level in actual practice.

Run 10 was a successful neutral elution run where the regeneration level was 240% of theory which resulted in an efficiency (E_M) of 0.42 and a final column capacity of 1.15 meq/ml for Duolite ES-368. The pH never dropped below 4.6, the carbonic acid pH, and could have been raised to near neutral by degasification to remove CO_2 .

Run 11 was also a successful neutral elution run, this time with Amberlite IR-45, a STY-DVB, polyamine resin with a much higher sulfate selectivity ($\alpha_N^S = 12.7$) than the STY-DVB tertiary amine resins represented by Duolite ES-368 ($\alpha_N^S = 2.83$). Furthermore, IR-45 is a gel resin with a higher, measured HCl capacity (1.76 meq/ml) than the macroporous ES-368 resin (1.43 meq/ml). At a regeneration level of approximately 300% of theory, 480 BV of Ca-Mg-Fe test water could be treated with an efficiency ($\bar{y}_N$)

of 0.44 and a final column capacity of 1.61 meq/ml. This was overall, the best performance of a weak base anion resin in neutral or acid elution if only E_M was considered as the performance criterion.

All three weak-base resins with high nitrate/chloride selectivity ($\alpha_{Cl}^N = 3.85$) performed acceptably in nitrate removal service irrespective of their sulfate/nitrate selectivities. Although no direct comparisons are possible from the experimental data the trends are clear and the calculated performance (91% of acid elution performance) of these resins in the proposed, two-bed system is summarized in Table 23 below:

TABLE 23. CALCULATED COLUMN PERFORMANCE OF WBA RESINS IN NITRATE REMOVAL SERVICE ON TEST WATER 3 ASSUMING 300% REGENERATION LEVEL

Resin	Final Column Capacity meq/ml	BV Treated	E_M
STY-DVB, Tert. Amine, MR	1.35	370	.42
STY-DVB, Polyamine, Gel	1.61	480	.44
Polyacrylic, Polyamine, Gel	2.84	840	.41

Clearly, there are minor differences among the efficiencies but large differences in capacities and bed volumes treated. As previously discussed, capacity per se doesn't influence the operating cost of a system except through the volume of rinses required per unit volume of water treated which should be high for low capacity resins. Nevertheless, if the highly sulfate selective resins do indeed require progressively longer rinses with time in service, then the capacity advantage is lost. A safe compromise might be the polystyrene polyamine resin with moderately high sulfate selectivity and the highest, maximum possible chemical efficiency ($E_M = .44$).

Bicarbonate Removal vs. Efficiency--

There was never any significant bicarbonate removal by the resins under any of the experimental conditions examined in this study. This was expected from the knowledge of the weak nature of carbonic acid ($pK_a = 6.3$); the uncharged H_2CO_3 species dominated at pH's below 6.3. Even during Run 7, the single-bed strong base anion run, there was only 1% HCO_3^- on the resin at the end of the run. This indicates the low selectivity the resin had for the HCO_3^- anion which was the dominant species during that run in which the pH of the feedwater was 7.4.

The fact that bicarbonate was nearly completely eluted before the nitrate breakthrough occurred enhanced the maximum possible chemical efficiency, E_M , for nitrate removal by reducing the total number of species present on the resin at the end of the run. Nevertheless, all resins removed H_2CO_3 completely from the first 40 to 200 bed volumes of effluent at 5 gal/min ft³ and some initial removal of HCO_3^- took place in the single bed, chloride form run (Run 7). When H_2CO_3 breaks through, the pH drops to near 4.5 which is unacceptably corrosive for a water supply. Usually, in a two-bed system, a degasifier would be installed between the cation and anion beds to remove CO_2 under the very acidic conditions produced by the mineral acids present. This may not be good practice here. A better location would probably be following rather than preceding the weak-base anion bed. Some beneficial kinetic effect due to the presence of H_2CO_3 in column experiments has been observed here and reported (I. Abrams, Diamond Shamrock Chemical Co., Personal Communication). Apparently in column operation H_2CO_3 is neutralized by the weak-base anions, whereupon the HCO_3^- anions are taken up thereby swelling the resin beads in the lower reaches of the bed where they compete with no other anion; finally, the swollen, bicarbonate-form resin takes up the next most preferred species (chloride) by rapidly exchanging the HCO_3^- for it. Simply stated, the bicarbonate anion is a catalyst for

the removal of the more preferred species in ion-exchange column operation. Thus it is questionable whether removing CO_2 from waters before anion-exchange in nitrate removal is good or bad design since the closer the approach to equilibrium the more chemically efficient is the operation of this process.

Comparative Process Economics

For a continuous, single-bed strong-base anion exchanger in nitrate removal service Holzmacher [66] estimated that the NaCl regenerant cost, plus the cost of regenerant brine disposal by trucking eight miles to a river before dumping, represented 50% of the operating costs of the process. That percentage can only increase when more expensive regenerants are used as in the two-bed system or when truly legitimate means are considered for sodium chloride brine disposal. With the two-bed system the cost for chemical regenerants will be higher but that increase will be offset by the nitrogen fertilizer value of those regenerants. The following economic analysis has been made with the conservative assumption that the two-bed regenerants wouldn't be sold, rather they would simply be given away to eliminate any disposal costs.

Table 24 compares the chemical costs of all the feasible regenerants for use single-bed and two-bed nitrate removal processes.

Assumptions Made in Regenerant Cost Calculations--

(1) Exhausted resin is 40% in the nitrate form at the end of a run. $E_M = 0.4$.

(2) Regenerants levels are 300% of theoretical: $E_R = .33$. In actual practice, sulfuric acid might have to be 400-500% of theoretical in high calcium waters due to CaSO_4 fouling and NaCl might have to be greater than 400% of theoretical in high sul-

fate waters.

(3) Raw water supply has approximate analysis of Test Water 3, Table 21 where $\text{NO}_3\text{-N}$ is 21 ppm, $C_T \approx .006 \text{ N}$, $\text{TDS} \approx 400$ ppm. Actually E_M and E_R won't change significantly at total concentrations up to about .06 N ($\text{TDS} \approx 4000$ ppm) if X_N remains constant, but the regenerant cost will increase or decrease in direct proportion to the total concentration (C_T) in meq/l.

(4) Chemical costs are calculated from published prices on August 2, 1976 in the Chemical Marketing Reporter. Prices are FOB production point, i.e., they don't include delivery which can be significant in remote locations. However, delivered ammonia costs will not be significantly higher than indicated due to the rather universal availability of anhydrous ammonia.

(5) Twenty-five percent of the raw water is bypassed for blending with the deionized water.

TABLE 24. CALCULATED CHEMICAL REGENERANT COSTS
(1 lb-equivalent = 14 lbs of nitrogen removed)

Regenerant Chemical	\$	¢	¢
	lb-equivalent	1000 gallon Treated	m ³ Treated
H_2SO_4	1.23	8.63	2.28
NaCl	1.30	9.15	2.42
NH_3	1.53	10.7	2.78
HCl	2.43	17.1	4.52
NH_4Cl	5.64	39.6	10.5
HNO_3	6.62	46.5	12.3

Only two of the above chemicals, NaCl and NH_4Cl , can be used in the single bed process while NH_3 and either HCl, HNO_3 or H_2SO_4 would have to be chosen for the two-bed process. Clearly, HNO_3

is very expensive compared to the other acids; furthermore, its use makes possible disastrous nitrate pollution of water supply should errors be made in valve switching during regeneration. In addition, the experimental runs demonstrated that inordinately long cation bed rinses would be required to bring the $\text{NO}_3\text{-N}$ concentration to below 1 ppm. Thus, nitric acid is not recommended even though it would much enhance the fertilizer value of the regenerants. Sulfuric acid is more economical, but if it must be used in 500% rather than 300% xs that advantage is lost to the relatively more expensive but more efficient HCl in calcium ion elution.

The further comparisons between the two-bed and single-bed processes in Table 25 are made with the following assumptions in addition to those already listed:

- 1) HCl and NH_4OH regenerants for the strong acid-cation and weak-base anion beds respectively.
- 2) NaCl regenerant for the strong-base anion column with disposal cost equal to regenerant cost. See Holzmacher [66, p. 212].
- 3) Regenerant volume for disposal comprises the actual regenerant plus one bed volume of displacement rinse. If all the rinses are collected for disposal and a value of 50 gal/ft³ (6.7 BV) is assumed for the rinse volume of each bed, the volume for disposal would approximately double and the solids concentrations would be correspondingly halved.

The regenerant plus disposal costs of the two-bed process are about 50% higher than the single-bed process but it is unlikely that the nitrate containing sodium salts from the single bed process will be permitted to be dumped at such low cost onto agricultural land or into any receiving waters except the oceans. A further disadvantage is that iron fouling of anion resins is known to be a problem in the single-bed process [10]

TABLE 25: ECONOMIC AND REGENERANT WASTEWATER COMPARISONS BETWEEN THE SINGLE-BED AND TWO-BED PROCESSES

Item	Single-Bed Process	Two-Bed Process
Regenerant Chemical Costs, ¢/1000 gal H ₂ O Supplied. . . .	9.2	27.8
Regenerant Chemical Costs, ¢/m ³ H ₂ O Supplied	2.43	7.34
Regenerant Disposal Costs, ¢/1000 gal H ₂ O Supplied . . .	9.2	Nil
Regenerant Disposal Costs, ¢/m ³ H ₂ O Supplied	2.43	Nil
Regenerant plus Disposal Costs, ¢/1000 gal H ₂ O	18.4	27.8
Regenerant plus Disposal Costs, ¢/m ³ H ₂ O Supplied	4.86	7.34
Regenerant Volume, % Total Water Supplied	0.78	1.73
Regenerant Composition: Total Concentration, N	1.08	0.650
Total Dissolved Solids, ppm	69,200	37,400
Undesirable Cation (Na ⁺), ppm	24,900	0
Calcium ion, ppm	0	2,480
Magnesium ion, ppm	0	465
Ammonium ion, ppm	0	8,780
Sulfate ion, ppm	7,870	3,540
Nitrate ion, ppm	8,960	4,030
Chloride ion, ppm	27,500	18,100
Nitrogen, ppm	2,020	7,740
Nitrogen Fertilizer Produced, lb N/1000 gal H ₂ O Supplied	0	1.12
Nitrogen Fertilizer Produced, kg/m ³ H ₂ O Supplied	0	.134
Per capita Fertilizer Production, lb N/capita·year . . .	0	40.9
Per capita Fertilizer Production, kg N/capita·year . . .	0	18.6

where significant reduction in efficiency and capacity have been observed. Some observations were made on that problem during the column experiments.

Seriousness of the Iron Fouling Problem

It was rather surprising to observe the volume of $\text{Fe}(\text{OH})_3$ produced from one ppm of ferrous iron upon oxidation by the air during experimental runs 9-11 in which the Ca-Mg-Fe test water was used. Admittedly the conditions were somewhat different than those which would prevail in a full-scale ground-water ion-exchange application as O_2 from the atmosphere was readily available whereas it would be less so in a closed, full-scale system. Nevertheless, some O_2 will be unavoidably introduced into the ion-exchange beds during the regeneration and rinsing steps; this oxygen will readily oxidize the ferrous iron and precipitate $\text{Fe}(\text{OH})_3$. In the two-bed system the iron hydroxide fouling was limited to the cation bed where it was, visibly at least, completely removed during regeneration with 1.5 N HCl as would be expected. This precipitated iron tended to cement itself, and clogged the first 10% of the cation bed and visibly penetrated 50% of that bed by the end of the run. The problem would have been very serious in a single-bed system if this amount of ferric iron had been involved. However, that was not experimentally substantiated here as there was no ferrous iron in the test water for the single bed run (Run 7). Beulow [10] emphasized the potential seriousness of this problem and reiterated the solution prescribed by the resin manufacturers, i.e., remove the iron before neutral, ion exchange. That would significantly increase the costs associated with the single-bed process reducing its relative cost advantage over the two bed process.

Organic Extractables in the Resins

Because there currently appears to be a good deal of justifiable concern over the presence of chlorinated hydrocarbon carcinogens in water supplies at the ppb level, the possible presence of organics leached from these synthetic organic ion exchangers must not be overlooked. While examining the UV spectra of acidic resin equilibrates during a search for possible interferences to the nitrate-by-UV method, a number of resins were observed to have produced what appeared to be very significant amounts of UV absorbing organics in the aqueous phase. To verify that these absorbance peaks in the 210 to 230 nm range were, in fact, due to organics, TOC analyses were run on 100 ml acidic (pH = 3) resin equilibrates tumbled for 20 hours with 1.00 gm of the various air-dried resins. The results of those analyses are listed in Table 26 below.

The only obvious trend in the data is that the STY- DVB, quaternary amine resins (Nos. 14-32) produced much less TOC than did the weak-base resins (Nos. 1-13). This may have been due to the chemical forms of the previously air-dried resins which were stored in tightly-capped, polyethylene bottles prior to the extraction experiment. The weak-base resins were stored in the free base form while the strong-base resins were stored in the more stable chloride form.

By far the worst resin as measured by UV contamination, visible contamination and TOC was the aliphatic polyamine resin Ionac A-260 (No. 11). Although not indicated in the table, two other anion resins produced visibly, yellow-colored waters at various times during the resin conditioning and batch equilibrium studies, these were the phenol formaldehyde polyamine resins: Duolites ES-561 and A-7. Also, the cation resin Amberlite IR-120 yielded an orange-colored supernatant water when stored in the hydrogen form. The point here is not so

much to cite particular resins as being unacceptable, but rather to point out that, visibly or invisibly, the organic contamination does exist with all resins to some degree at least when they are relatively new.

TABLE 26. ORGANIC LEACHED FROM "CONDITIONED" ANION RESINS

U-M Resin No.	Description	ppm TOC
1	STY-DVB, Tertiary Amine, MR	14
2	Acrylic-Amine, Tertiary Amine, GEL	5
3	STY-DVB, Polyamine, GEL	35
4	Epoxy-Amine, Polyamine, GEL	13
5	STY-DVB, Tertiary Amine, MR	16
6	Phenol-HCHO, Polyamine, MR	26
7	Epoxy-Amine Polyamine, GEL	25
8	STY-DVB, Tertiary Amine, MR	46
9	Phenol-HCHO Polyamine, MR	30
10	Acrylic Amine, Polyamine, MR	20
11	Aliphatic Amine, Polyamine, GEL	90
12	STY-DVB, Tertiary Amine, MR	33
13	Epoxy-Amine, Polyamine, GEL	19
14	STY-DVB, Quat. (II) Amine, MR	8
16	STY-DVB, Quat. (I) Amine, ISO	6
17	STY-DVB, Quat. (I) Amine, MR	4
21	STY-DVB, Quat. (I) Amine, GEL	3
32	STY-DVB, Quat. (I) Amine, MR	4

RESIN CONCENTRATION $\approx$ 0.9%

EXPOSURE TIME: 16 HOURS IN A 13 RPM TUMBLER

TEMPERATURE: 25°C

pH $\leq$ 2.5 (HCl)

INSTRUMENT: MODEL 915 BECKMAN TOC ANALYZER

Many of the TOC values were alarmingly high in spite of the fact that exposure time was 16 hours compared to the short 1 to 3 minutes typical detention time in an ion-exchange column. Also, there was the possibility of organic particulates from resin attrition due to tumbling -- a non-representative condition with respect to column behavior. Nevertheless, one must be concerned with these values as they are thousands of times higher than the desirable levels even after the resins had been "conditioned" by extensive backwashing and two service cycles with 1.0 N NaOH and 1.5 N HCl including the appropriate, intermediate and final rinses. Resin manufacturers are aware of this problem; Rohm and Haas [106] draws attention to it and recommends a solution to be used in treating resins for use in food and drug processing:

"Furthermore, Amberlite IR-45 contains trace quantities of low molecular weight aromatic hydrocarbons which are leached slowly from resin during service unless properly pretreated...A most effective way in which the residual aromatic material can be removed is to place the resin in a column and pass steam at atmospheric pressure down through the column allowing the condensate to drain freely at the bottom. Ordinarily a matter of several hours of such treatment after the entire bed has reached steam temperature is sufficient to remove virtually all the aromatics as well as any residual traces of free amines and low molecular weight amino compounds which may be left in the resin at the conclusion of the manufacturing process."

Such a procedure would seem to be highly recommended for resins prior to usage in water supply. Even so, the existence of such a recommended solution doesn't eliminate what appears to be a real need for research on the identification and quantification of the organics leached from ion-exchange resins in water supply applications. One final note: the TOC results

were highly variable and tended to change upon standing so care must be exercised in the design of truly quantitative experiments. The loss of volatile organics must be avoided as that seemed to be one cause of the variability.

PHASE II RESULTS SUMMARY: MULTICOMPONENT CHROMATOGRAPHIC COLUMN STUDIES

Nitrate/Chloride selectivity (α_{Cl}^N) is the most important selectivity in determining the relative amount of nitrate on the resin at nitrate breakthrough, i.e., in determining the maximum possible chemical efficiency (E_M or $\bar{y}_N$). This is both good and bad: good because all the resins were nitrate selective with respect to chloride; bad because little variation existed in the values of α_{Cl}^N among the thirty-two resins tested ($\alpha_{Cl}^N = 1.85 - 4.33$) and no real significant effects on selectivity seem possible by further varying the important independent variables--matrix and relative degree of crosslinking.

Sulfate/nitrate selectivity (α_N^S) is nearly irrelevant in determining the average equivalent fraction of nitrate on the resin at the end of a run ($\bar{y}_N$). Surprisingly, slight increases in $\bar{y}_N$ are possible as a result of increasing rather than decreasing the sulfate selectivity-- α_N^S . The simple explanation offered for this is that (1) all the sulfate will be removed from the feedwater regardless of its actual selectivity because it is the most preferred species and (2) high sulfate selectivity promotes a short sulfate-rich zone near the column entrance in which almost no nitrate is removed thereby leaving essentially all of that species to compete with the lesser preferred chloride in the second equilibrium zone of the column which is where nearly all of the nitrate is concentrated; see Fig. 5. Regardless of the explanation, the effect of the selectivity of the most preferred species, sulfate, is predictably slight when the objective is to remove nitrate, invariably the lesser-preferred

species.

E_M the maximum possible chemical efficiency in nitrate removal service has been defined as being equal to the average equivalent fraction of nitrate on the exhausted resin ($\bar{y}_N$). This $\bar{y}_N$ will be greater than x_N if the resin concentrates nitrate by eluting the lesser preferred species (H_2CO_3 and Cl) in chromatographic fashion until nitrate breakthrough. As has just been discussed $\bar{y}_N$ is not much influenced by α_N^S and only moderately influenced by α_{Cl}^N because of the narrow range of values possible for α_{Cl}^N among commercially available resins. The most important influence on $\bar{y}_N$ is, predictably, x_N ; when it's low, process efficiency will be correspondingly low because the exhausted resin will comprise mostly sulfate and chloride--species not intended to be removed; see Fig. 29. In these studies the influence of x_N , at 2.5 gal/min ft³, $\alpha_{Cl}^N = 3.9$ and $x_S = 0.3$ was as follows:

Liquid Phase Equivalent Fraction of Nitrate	Resin Phase Average Equivalent Fraction of Nitrate	Relative Efficiency
x_N	$\bar{y}_N$	$\bar{y}_N/x_N$
.20	.32	1.70
.27	.40	1.48

Relative efficiency has been included to illustrate that $\bar{y}_N$ is not simply linearly related to x_N . In addition to α_{Cl}^N and x_N , the interrelated variables, exhaustion rate, bed depth and superficial detention time (τ), are quite significant. Short detention times ($\tau < 3.0$ min), shallow beds (depth < 60 cm) and high exhaustion rates (> 2.5 gal/min ft³) reduce $\bar{y}_N$ by causing relatively more chloride, apparently the kinetically favored anion, to be in the resin at nitrate breakthrough. That is summarized below for the condition where $x_N = .27$, $x_S = .27$, $x_{Cl} = .27$ and $\alpha_{Cl}^N = 3.9$:

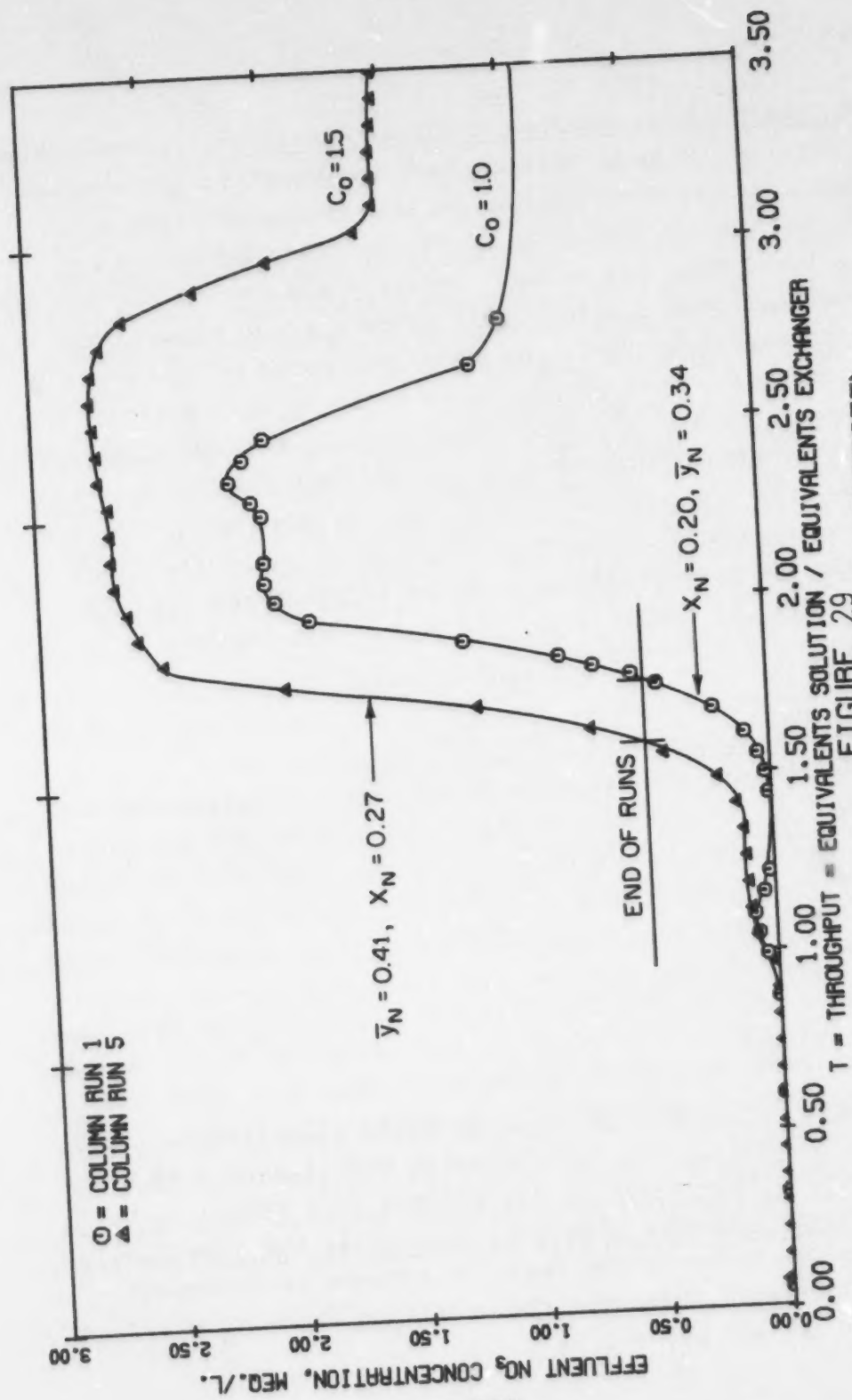


FIGURE 29
 COLUMN EFFLUENT PROFILES (NITRATE)
 EFFECT OF NITRATE CONCENTRATION ON COLUMN EFFICIENCY

<u>Exhaustion Rate</u> <u>gal/min ft³</u>	<u>τ</u> <u>min</u>	<u>Resin</u> <u>Depth</u> <u>cm</u>	<u>$\bar{y}_N$</u>
2.44	3.1	61	.41
4.88	1.5	31	.39

Although x_S was not a variable in the column experiments it will greatly influence $\bar{y}_N$ because all the sulfate fed to the column will still be on it at nitrate breakthrough. When x_S is high, the efficiency, $\bar{y}_N$, will be low.

Regeneration level influenced both the overall chemical efficiency (E_O) and the maximum possible chemical efficiency (E_M). For the two-bed system, the regeneration level has been defined based on the final anion column capacity. In practice, the total equivalent capacity (TEC) of the cation bed must equal or exceed the final anion bed capacity. It has been determined here that a regeneration level of 300% of the theoretical HCl required must be applied to the cation bed if calcium and magnesium are the primary cations on the resin. Levels much lower than that cause premature cation breakthrough, increased pH and reduced anion bed capacity with smaller values of $\bar{y}_N$ at breakthrough. High regeneration levels on the other hand maximize $\bar{y}_N$ but cause unacceptably low effluent pH forcing termination of the run. For each specific groundwater application the sizes of the beds and the exact regeneration level would have to be determined to insure maximum $\bar{y}_N$ and a neutral process effluent.

For the single-bed strong-base anion process regenerated with NaCl it is expected that regeneration levels of 300% or greater will be required for efficient regeneration. This is based on published rather than experimentally determined information.

Net bicarbonate removal was zero, as expected for both the two-bed and single-bed processes. Thus, high values of bicarbonate in the raw water don't measurably influence $\bar{y}_N$. Bicarbonate and carbonic acid apparently have a catalytic effect in columnar ion-exchange processes so it is tentatively recommended that the system degasifier be placed downstream from the anion bed rather than preceding it.

The effluent concentration profiles at 2.5 gal/min ft³ were very sharp but not quite vertical indicating that, at the end of the run, nitrate breakthrough can be readily anticipated and used to control the process. Unusually shaped profiles with early and inefficient nitrate breakthrough resulted from premature pH increases in the weak-base anion column influent due to insufficient cation bed capacity.

The final column capacities and bed volumes of effluent to nitrate breakthrough were of course, very much a function of the advertised and measured capacities of the resins and the sulfate concentrations of the feed waters. High column capacities can improve the overall economic efficiency of an ion-exchange process if they lead to lower rinse volume requirements but, since high capacity resins also tend to be highly sulfate selective and require progressively longer rinse volumes with service time, that possible improvement in operating efficiency is not guaranteed.

To compute the expected multicomponent column capacity of a highly sulfate selective resin at nitrate breakthrough one should assume that all the sulfate will be removed, and use the advertised or measured H_2SO_4 capacity (see Titration Curves, Figs. B1-B13) for that fraction of the capacity represented by sulfate ions, and do likewise for HCl and HNO_3 taken together assuming in all cases that insignificant H_2CO_3 will be on the resin at the end of the run. The equation is as follows; It

assumes that HCl capacity = HNO_3 capacity:

Expected Multicomponent Column Capacity = $(x'_S) (\text{H}_2\text{SO}_4 \text{ Cap.}) + (1-x'_S) (\text{HCl Cap.})$

where x'_S = Equivalent fraction of $\text{SO}_4^{=}$ in raw water not including HCO_3^- . For Test Waters 2 and 3, $x'_S = 0.33$.

The overall chemical efficiency (E_O) can be expected to be about 13.3% for both the single-bed and two-bed processes. This is based on the observed average equivalent fraction of nitrate on the resin at the end of the runs ($\bar{y}_N$) with a feedwater containing the same equivalent concentration of nitrate, chloride and sulfate and an irrelevant amount of bicarbonate which undergoes no net removal in either process. This overall chemical efficiency has been defined as the equivalents of nitrate removed per equivalent of regenerant supplied and is the product of $\bar{y}_N$ (or E_M) and E_R , the regeneration efficiency, which has been determined to be 0.33 based on a regeneration level of 300%.

A comparative process economic evaluation reveals that the two-bed process with NH_3 and HCl as regenerants has chemical plus disposal costs which are approximately 50% higher than the single-bed process assuming an overall chemical efficiency of 13.3%, 25% bypass water, a feedwater with the composition of Test Water 3 (Table 21), NaCl- NaNO_3 brine disposal by trucking 8 miles before discharging into a stream, and no disposal cost for the high-nitrogen content wastewaters from the two-bed process which are given away for their fertilizer value. See Tables 24 and 25 for complete details of the comparative economic evaluation.

The advantages (+) and disadvantages (-) of the single-bed and two-bed processes are as follows:

Single-bed, strong-base anion with NaCl regeneration

- (+) Simple, no balancing of beds and regenerants
- (+) Low cost regeneration
- (-) Very difficult and costly to dispose of regenerants in non-coastal locations where natural evaporation is impossible
- (-) Iron must be removed to prevent resin fouling
- (-) Continuous nitrate analysis required for process control

Two-bed, strong-acid, weak-base NH_3 & HCl regenerants

- (+) Partial softening in addition to nitrate removal
- (+) No problem with iron fouling. Precipitated iron is removed from the cation bed during each regeneration
- (+) Regenerant wastewaters expected to be easy to dispose of by land application as fertilizer
- (-) Complex system: bed sizes and regenerants must be balanced
- (-) Degasifier for CO_2 removal required
- (-) Continuous pH and nitrate analysis required for process control
- (-) High regenerant costs

Continuous ion-exchange processes of the pulsed-resin flow type will be more difficult to control in chromatographic elution to nitrate breakthrough because there will be a nitrate breakthrough prior to every resin pulsing operation. That will require a control decision based on nitrate analysis once every few minutes compared to the once or twice-per-day decision for a large fixed-bed operation. An efficient, continuous, two-bed system of the type recommended here would seem to be unduly complicated because of the requirements for balanced capacities and chromatographic elution of both beds.

Organic extractables present in the anion resins even after "conditioning" gave rise to total organic carbon (TOC) concentrations in the 3-100 ppm range in acidic, aqueous solutions containing about 0.9% resin agitated for 16-20 hours. It is anticipated that the extractable organics in both cation and anion resins represent a potential problem in water supply. Research on the ppb level of organics associated with the existing and potential uses of ion exchangers in water supplies definitely seems warranted in view of this TOC data and the recent concern over organics in public water supplies.

Nitric acid is definitely not recommended as a regenerant in the two-bed process even though it would greatly enhance the fertilizer value of the regenerant wastewaters. It is too costly, 46.5¢/1000 gal treated water ($12.3¢/m^3$), requires excess cation bed rinsing to reduce nitrate and allows the possibility of disastrous nitrate and acid pollution of the water supply in the even of an operating error. Even though HCl is more costly than H_2SO_4 it may be more economical where large excesses of H_2SO_4 are required due to $CaSO_4$ fouling of the cation bed.

A ranking of anion resins for nitrate removal service is given in Table 27, considering that high nitrate/chloride selectivity high capacity and moderate sulfate/nitrate selectivity are the desirable characteristics. Organic extractables as evidenced by the TOC of resin equilibrates were not considered in making the rankings because of the very preliminary nature of those measurements. However, an asterisk (*) has been used to indicate a resin producing markedly colored water in addition to high TOC.

Although the resins are ranked in preference order, the differences among the recommended resins are not large; they are all expected to give nearly the same maximum possible chemical efficiency E_M . Some overall process efficiency is gained by

using high capacity resins while some might be lost with the highly sulfate selective resins should they require rinse volumes.

TABLE 27
RANKING OF RESINS FOR USE IN NITRATE REMOVAL SERVICES

Recommended
STY-DVB, Polyamine Resins Amberlite IR-45
STY-DVB, Tertiary-amine, MR Resins Amberlite IRA-93 Dowex MWA-1 Ionac AFP-329 Duolite ES-368
STY-DVB, Quat. (I & II) Amines, Gel & MR Resins Ionac ASB-100, AFP-100, A-641, ASB-1P, ASB-2 Duolite, A-101-D, A-102-D Dowex 11, SAR, SBR-P, SBR Amberlite IRA-400, IRA-900, IRA-402, IRA-910, IRA-410
Acrylic-Amine, Polyamine, MR Resins Duolite ES-374
Phenol-HCHO, Polyamine, MR Resins Duolite A-7 Duolite ES-561
Not Recommended
Epoxy-amine, Polyamine, Gel Resins Dowex WGR Duolite A-340 Ionac A-305
Acrylic-Amine, Tertiary Amine, Gel Resins Amberlite IRA-68
Aliphatic-Amine Polyamine, Gel Resins *Ionac A-260

REFERENCES

1. Adams, G., P.M. Jones, and J.R. Millar, "Kinetics of Acid Uptake by Weak-Base Anion Exchangers" J. The Chemical Society, Inorg. Phys. Theor., p. 2543, (1969).
2. American Public Health Association, American Water Works Pollution Control Federation, Standard Methods for the Examination of Water and Wastewater, 13th Ed., American Public Health Assoc., Washington, D.C. 20036, 1971.
3. American Water Works Association, Water Quality and Treatment - A Handbook of Public Water Supplies, 3rd Ed., McGraw-Hill Book Co., Inc., New York, N.Y., 1971, Chapter 10.
4. Ames, L.L., "Some Zeolite Equilibria with Alkaline Earth Metal Cations" American Mineralogist, V. 49, p. 1099, (1964).
5. Ames, L.L., "Zeolite Cations Selectivity," Canadian Mineralogist, V. 8, p. 325, (1965).
6. Anderson, R.E. "On the Pickup of Hydrochloric and Sulfuric Acids on a Polyamine Resin" in Polyelectrolytes and Their Applications p. 263, D. Reidel Publishing Co., Dordrecht-Holland, 1975.
7. Anderson, R.E., "A Countour Map of Anion Exchange Resin Properties" I&EC Product Res. & Dev., V. 3(2), p. 85, June 1964.
8. Aveni, A., G. Boari, L. Liberti, M. Santori and B. Monopoli, "Sulphate Removal and Dealkalization on Weak Resins of the Feed Water for Evaporation Desalting Plants." Desalination, V. 16, p. 135 (1975).
9. Baumann, W.C., in Ion Exchange: Theory and Application, Editor F.C. Nachod, Academic Press Inc., New York, 1949.
10. Beulow, R.W., K.L. Kropp, J. Withered, and J.M. Symoné, "Nitrate Removal by Anion Exchange Resins," Water Supply Research Laboratory, National Environmental Research Center, U.S. EPA, Cincinnati, Ohio, May, 1974.
11. Bingham, E.C., "Fertilizer Maker Stops Nitrogen," Water and Wastes Engineering, P.E-4, November, 1972.

12. Blalock, H.M., Social Statistics, 2nd. Ed., McGraw-Hill, New York, (1972).
13. Boari, G., L. Liberti, C. Merli and R. Passino, "Exchange Equilibria on Anion Resins," Desalination, V. 15, p. 145-166, 1974.
14. Bolto, B.A. and R.E. Warner, "An Ion-Exchange Process with Thermal Regeneration VII. The Rates of Neutralization of Weak Electrolyte Resins." Desalination, V. 8, p. 21-34, 1970.
15. Bolto, B.A., "Sirotherm Desalination: Ion Exchange with a Twist" Chemtech, p. 303, May 1975.
16. Bouwer, Herman; "Renovating Municipal Wastewater by High-Rate Infiltration for Ground-Water Recharge" Journal AWWA, p. 159, March, 1974.
17. Bouwer, Herman; R.C. Rice, and E.D. Escarcenga; "Renovating Secondary Sewage by Ground Water Recharge with Infiltration Basins", U.S. Environmental Protection Agency, Water Pollution Control Res. Series, 16060 DRV, U.S. GPO, 1972.
18. Boyd, G.E., J. Schubert, and A.W. Adamson, The Exchange Adsorption of Ions From Aqueous Solutions by Organic Zeolites. I. Ion-Exchange Equilibria." J. ACS, V. 69, p. 2818, Nov. 1947.
19. Boyd, G.E., A.W. Adamson, and L.S. Myers, Jr., "Ion-Charge and Exchange Rates with Ion-Exchange Polymers." J. ACS, V. 72, Oct. 1950.
20. Boyd, G.E. and B.A. Soldano, Self-Diffusion of Cations in and Through Sulfonated Polystyrene Cation-Exchange Polymers, J. ACS, V. 75, No. 24, p. 6091, Jan., 1954.
21. Boyd, G.E., A.W. Adamson, and L.S. Myers, Jr., "The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. II. Kinetics" J. ACS, V. 69, p. 2836, Nov. 1947.
22. Bregman, J.I., and J.M. Schackelford, "Ion-Exchange is Feasible for Desalination" Environmental Sci. & Tech., Vol. 3, No. 4, p. 336, 1969.
23. Case, A.A., "The Health Effects of Nitrates in Water" Proc. 12th Sanitary Engineering Conf., Univ. of Ill., Urbana, Ill., February, 1970.

24. Chemerys, J.C., "Effect of Urban Development on the Quality of Ground Water in Raleigh North Carolina, USGS Professional Paper 575-B, pp. 212-216 (1967).
25. Chemical Marketing Reporter, Schnell Publishing Co., August 8, 1976.
26. Chu, B., D.C. Whitney and R.M. Diamond, "On Ion-Exchange Resin Selectivities," J. Inorg. Nucl. Chem., V. 24, p. 1405, 1962.
27. Clazie, R., "Multicomponent Diffusion: Generalized Theory, With Ion-Exchange Applications" Ph.D. Thesis, Univ. of California, Berkeley, 1967.
28. Clifford, D.A., "Feasibility Study for Total Water Management at Arcosanti Arizona" Report to the Cosanti Foundation, University of Michigan, April 29, 1974.
29. Cole, J.A., Editor, Groundwater Pollution in Europe, Proceedings of a conference organized by the Water Research Association, in Reading, England, September 1972, Water Information Center, Port Washington, N.Y., (1974).
30. Conway, D.E., J.H.S. Green and D. Reichenberg, "The Kinetics of Sodium-Hydrogen Exchange on a Monofunctional Cation Exchange Resin Containing Carboxyl Groups", Trans. Faraday Soc., V. 50, p. 511, 1954.
31. Copeland, J.P., C.L. Henderson, J.M. Marchello, "Influence of Resin Selectivity on Film Diffusion Controlled Ion-Exchange" A.I.Ch.E.J., Vol. 13, No. 3, May 1967, p. 449-52.
32. Copeland, J.P. and J.M. Marchello, "Film Diffusion Controlled Ion-Exchange with a Selective Resin," Chem. Eng. Sci., Vol. 24, No. 9, Sept. 1969, p. 1471-4.
33. Crabtree, K.T., "Nitrate Variation in Ground Water," Univ. of Wisconsin (Madison), Water Resources Center, Supplemental Report, 1970.
34. Dean, J.A. (Editor), Lange's Handbook of Chemistry, Sections 5 & 6 - Analytical Chemistry & Electrochemistry, 11th Ed., McGraw-Hill, New York, (1973).
35. deLaguna, W., Chemical Quality of Water - Brookhaven National Laboratory and Vicinity, Suffolk County, New York, USGS Bull., 1156-D (1964).
36. Diamond Shamrock Chemical Co., Duolite Ion-Exchange Manual, Redwood City, CA, 1969.

37. Diamond Shamrock Chemical Co., "Duolite Ion Exchange Resins - List of Products Properties and Uses" Redwood City, CA., 1970.
38. Diamond, R.M., "The Aqueous Solution Behavior of Large Univalent Ions. A New Type of Ion-Pairing", J. Phys. Chem., V. 67, p. 2513, Dec. 1963.
39. Diamond, R.M., and D.C. Whitney, "Resin Selectivity in Dilute To Concentrated Aqueous Solutions" in Ion Exchange: A Series of Advances, J.A. Marinsky Ed., Marcel Dekker Inc., New York, 1966.
40. Dorfner, K., Ion Exchangers: Properties and Applications, 3rd Ed., Ann Arbor Science, Ann Arbor, Mich., (1972).
41. Dow Chemical Co., "Laboratory Manual on Ion-Exchange" The Dow Chemical Co., Midland, Michigan, 1971.
42. Draper, N. and H. Smith, Applied Regression Analysis, Wiley, New York, (1968).
43. Eiseman, G., "Cation Selective Glass Electrodes and Their Mode of Operation", Biophysical J., V. 2, p. 259, (1962).
44. Eliassen, R., B.M. Wyckoff and C.D. Tonkin; "Ion-Exchange for Reclamation of Reusable Supplies" J. AWWA, pp. 1113-22, Sept., 1965.
45. Eliassen, R. and G.E. Bennett; "Anion Exchange and Filtration Techniques for Wastewater Renovation", J. WPCF, Vol. 39, No. 10, Part 2, pp. R 82-91, 1967.
46. Eliassen, R. and Tchobanogeous, "Chemical Processing of Wastewater for Nutrient Removal" J. WPCF, Vol. 40, No. 5, part 2, p. R 172, 1968.
47. Evans, S., "Nitrate Removal by Ion-Exchange" J. WPCF, V. 45, No. 4, pp. 632-36, April, 1973.
48. Fox, D.J. and K.E. Guire, "Documentation for MIDAS: Michigan Interactive Data Analysis System, 2nd. Ed., Univ. of Michigan Statistical Research Laboratory, Ann Arbor, Mich., (1973).
49. Gauntlett, R.B., "Nitrate Removal from Water by Ion-Exchange" Water Treatment and Examination, V. 24, p. 172, (1975).
50. George, W.O., and Hastings, W.W., "Nitrate in the Ground Water of Texas", Trans. of Am. Geophys. Union, V. 32, No. 3, pp. 450-456, (1951a).

51. Gold, H. and A. Todisco, "The Avco Continuous Moving Bed Ion-Exchange Process and Large Scale Desalting", Desalination, 17 (1975), p. 97.
52. Graham, E.E. and Dranoff, J.S., "Kinetics of Anion Exchange Accompanied by Fast Irreversible Reaction" A.I. Ch.E. Journal Vol. 18, No. 3, May (1972).
53. Gregg, J.C., "Nitrate Removed at Water Treatment Plant", Civil Engineering - ASCE, p. 45, April (1973).
54. Gregory, J. and R.V. Dhond, "Anion Exchange Equilibria Involving Phosphate, Sulfate and Chloride", Water Research, V. 6, 1972, pp. 695-702.
55. Grinstead, R.R. and K.C. Jones; "Nitrate Removal from Waste Waters by Ion-Exchange", Environmental Protection Agency Water Pollution Control Research Series No. 17010 FSJ, U.S. GPO, Washington, D.C., Jan., 1971.
56. Grinstead, R.R., R.M. Wheaton, T.E. Drisko and K.C. Jones, "Feasibility of Removal of Nitrates from San Luis Drain Waters by Ion Exchange" Report by the Dow Chemical Co. to U.S. Dept. of Interior: Bureau of Reclamation, STS No. PB180342, Oct. 9, 1968.
57. Guttman, I., S.S. Wilks, J.S. Hunter, Introductory Engineering Statistics, 2nd Ed., John Wiley, New York, (1971).
58. Hall, E.S., "Some Chemical Principles of Groundwater Pollution" in Groundwater Pollution in Europe, J.A. Cole, Editor, Water Information Center, Port Washington, N.Y. (1974).
59. Harned, H.S. and B.B. Owen, The Physical Chemistry of Electrolytic Solutions, ACS Monograph Series No. 137, 3rd Ed. Reinhold, New York (1958).
60. Helfferich, Friedrich, Ion Exchange, McGraw-Hill Book Co. Inc., New York, N.Y., 1962.
61. Helfferich, F., "Ion Exchange Kinetics," in Ion Exchange: A Series of Advances, Vol. 1, J.A. Marinsky Ed., Marcel Dekker Inc., New York, 1966.
62. Helfferich, F., "Ion-Exchange Kinetics. v. Ion Exchange Accompanied by Reactions," J. Phys. Chem., V. 69, p. 1178, 1965.
63. Helfferich, F.G., "Multicomponent Ion Exchange in Fixed Beds" I&EC Fund., V. 6, No. 3, p. 362, (1967).

64. Helfferich, F. and G. Klein, Multicomponent Chromatography: Theory of Interference, Marcel Dekker, New York, 1970.
65. Hering, B., and B. Harding, "Diffusion in Ion-Exchange Resins" A.I.Ch.E.J., Vol. 9, No. 4, p. 495, 1963.
66. Holzmacher, R.G., "Nitrate Removal from a Ground Water Supply" Water and Sewage Works, p. 210, July, 1971.
67. Huckel, W., Structural Chemistry of Inorganic Compounds, Elsevier Publ. Co., New York, 1951.
68. International Atomic Energy Agency, "Operation and Control of Ion-Exchange Processes for Treatment of Radioactive Wastes", IAEA, Tech. Report Series No. 78, Vienna, Austria, 1967.
69. Jensen, C.H., and R.M. Diamond, "Anion Exchange in Concentrated Solutions", J. Phys. Chem., V. 69, No. 10, p. 3440, 1965.
70. Klein, G., M. Villena-Blanco, T. Vermeulen, Ind. Eng. Chem., Process Design and Development, V. 3, p. 280, (1964).
71. Klein, G., D. Tondeur, T. Vermeulen, "Multicomponent Ion Exchange in Fixed Beds", I&EC Fund., Vol. 6, No. 3 p. 339 (1967).
72. Korngold, E., "Removal of Nitrates from Potable Waters by Ion-Exchange" Water, air, Soil Pollution, Vol.2, No. 1, pp. 15-22, 1973, CA 79:45602.
73. Kreusch, E., and K. Schmidt, "Wastewater Demineralization by Ion-Exchange", Environmental Protection Agency, Water Pollution Control Research Series No. 17040 EEE, U.S. GPO. Washington, D.C., Dec. 1971.
74. Kunin, R., and R.J. Myers, "Rates of Ion Exchange in Ion Exchange Resins", J. Phys. and Colloid Chem. Vol. 51, No. 5, pp. 1111, (1947).
75. Kunin, R., and R.J. Myers, "The Anion Exchange Equilibria in an Anion Exchange Resin", J. ACS, V. 69, p. 2874 (1947).
76. Kunin, R and R.E. Barry, "Carboxylic, Weak-Acid Type Cation Exchange Resin" Ind. Eng. Chem., V. 41, p. 1269 (1949).
77. Kunin, Robert and R.J. Myers, Ion-Exchange Resins, John Wiley & Sons, Inc., New York, pp. 57-58, (1950).

78. Kunin, Robert; Ion Exchange Resins, 2nd Ed., John Wiley & Sons, Inc., New York, 1958.
79. Lehmann, E.J., Ground Water Pollution, Part 2 Pollution from Irrigation and Fertilization, NTIS No. PS-75/740, U.S. Dept. of Commerce, Springfield, Va., Sept. (1975).
80. Liberti, L. and R. Passino, "Chloride-Sulphate Exchange on Anion-Exchange Resins Kinetic Investigations. I." J. Chromatography, V. 102, p. 155, 1975.
81. Lupa, Alan J., "The Kinetics of Ion-Exchange With Simultaneous Film and Particle Diffusion," Ph.D. Thesis, Chem. Eng., Northwestern Univ., 1967.
82. Marinsky, J.A., "Prediction of Ion-Exchange Selectivity" J. Phys. Chem., Vol. 71, NO. 6, p. 1572 (1967).
83. Mathews, A.P., "Mathematical Modelling of Multi-component Adsorption in Batch Reactors", Ph.D. Thesis, Univ. of Michigan, Ann Arbor, 1975.
84. McKee, J.E. and H.W. Wolf; Water Quality Criteria, 2nd Ed., 1963, State Water Resources Control Board, Sacramento, CA., Publication 3-A, April, 1971.
85. Meloan, C.E., "The Selective Removal of Nitrate and Nitrite from Polluted Water," Prepared for Office of Water Resources Research, NTIS No. PB-231471, U.S. Dept. of Commerce, Springfield, Va., March 1974 .
86. Midkiff, W.S., "Reactions of a Strongly Basic Ion-Exchange Resin in Dilute Aqueous Solution in a Columnar System", Ph.D. Thesis, University of Mich., Ann Arbor, 1969.
87. Midkiff, W.S., and Weber, W.J., Jr., "Operating Characteristics of Strong-Base Anion Exchange Reactors" Proceedings of the 25th Purdue Industrial Waste Conference, May, 1970.
88. Moison, R.L., and H.A. O'Hern, Jr., "Ion-Exchange Kinetics" Chem. Eng. Prog. Symposium Series, V. 55, No. 24, p. 71, 1959.
89. Moore, W.J., Physical Chemistry, Third Ed., Prentice-Hall, Inc., Englewood Cliffs, N.J., (1962).
90. Naber, J.E., and Wesseligh, J.A., "New Shell Process Treats Claus Off-Gas", CEP, V. 69, No. 12, p. 29, Dec., 1973.

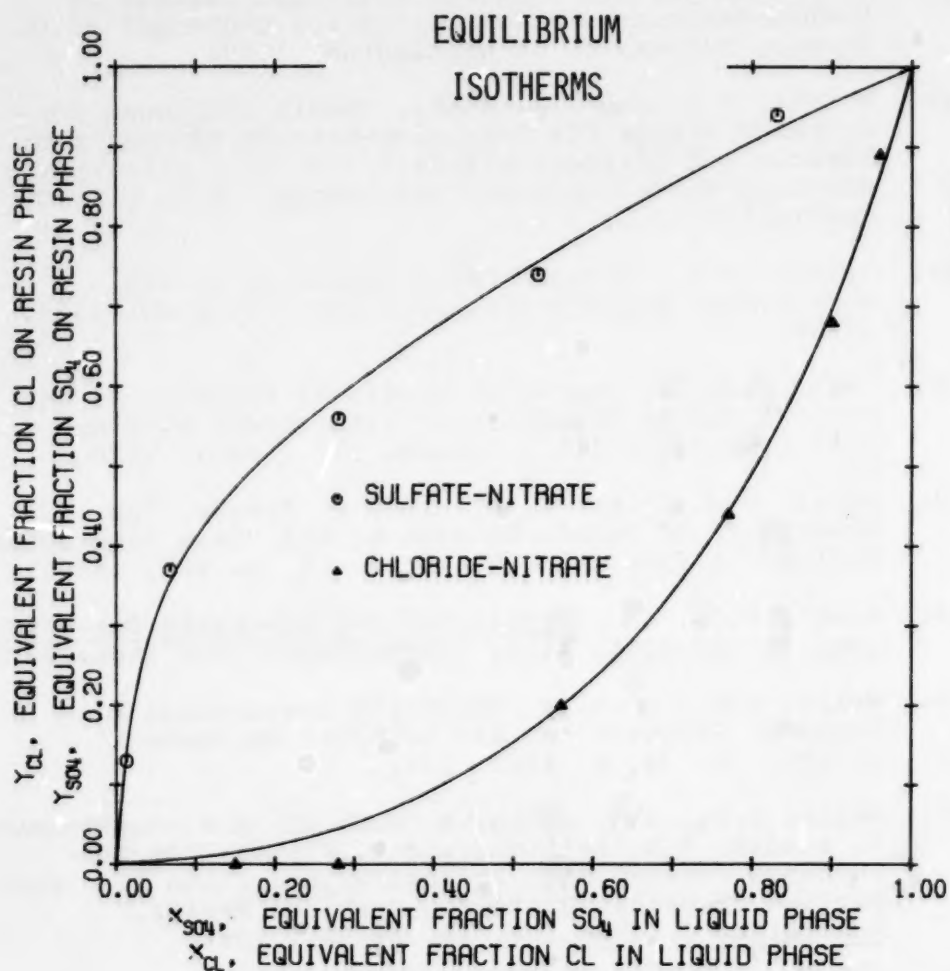
91. National Academy of Sciences Committee on Nitrate Accumulation; Accumulation of Nitrate, Washington, D.C., 1972.
92. National Academy of Sciences and National Academy of Engineering, "Water Quality Criteria 1972" Report of Committee on Water Quality Criteria, Environmental Studies Board NAS-NAE, EPA Ecological Research Series No. EPA-R3-73-033, U.S. GPO, Washington, D.C., March, 1973.
93. Nightingale, H.I., "Statistical Evaluation of Salinity and Nitrate Content and Trends Beneath Urban and Agricultural Area--Fresno, Calif.," Ground Water, V. 8, No. 1, pp. 22-28 (1970).
94. O'Brien, W.J., "Chemical Removal of Nitrate from Potable Water Supplies" Kansas Water Resources Research Institute, Manhattan, Kansas, June (1968).
95. Osborn, G.H., Synthetic Ion Exchangers, Chapman & Hall Ltd., London, p. 16 (1961).
96. Palmquist, W.N., and F.R. Hall, "Reconnaissance of Ground Water Resources in the Blue Grass Region, Kentucky", USGS, WSP 1833, (1961).
97. Paterson, R., An Introduction to Ion Exchange, Heyden and Son Ltd., London, 1970.
98. Pauling, L., The Nature of the Chemical Bond, Cornell University Press, 1960.
99. Peroni, L.J., and J.S. Dranoff, "Ion-Exchange Equilibria in a Ternary System" A.I.Ch.E.J., Vol. 9, No. 1, p. 42, 1963.
100. Perry, J.H., et. al., Chemical Engineers Handbook, 5th Ed., Chapter 16, "Adsorption and Ion Exchange" McGraw Hill, New York (1974).
101. Rao, M.G. and M.M. David, "Single-Particle Studies of Ion-Exchange in Packed Beds: Cupric Ion-Sodium System," A.I.Ch.E.J., V. 10, No. 2, p. 213, 1964.
102. Reddy, M.M. and J.A. Marinsky, "Ion-Exchange Selectivity Coefficients in the Exchange of Calcium, Strontium Cobalt, Nickel Zinc and Cadmium with Hydrogen Ion in Various Crosslinked Polystyrene Sulfonate Cation Exchangers at 25° C", J. Macromol. Sci-Phys., V. B5(1), p. 135, March 1975.

103. Reichenberg, D., "Ion-Exchange Selectivity" in Ion Exchange: A Series of Advances, J.A. Marinsky Ed., Marcel Dekker, Inc., New York, 1966.
104. Rohm and Haas Co. Inc., Engineering Manual for the Amberlite Ion-Exchange Resins, Philadelphia, PA., 1970.
105. Rohm & Haas, Technical Bulletin: Amberlite IR-120 Plus, The Rohm & Haas Co. Philadelphia, PA., Sept. 1972.
106. Rohm & Haas, Technical Bulletin: Amberlite IR-45 Technical Notes, The Rohm and Haas Co., Philadelphia, PA., Feb. 1971.
107. Sabadell, J.E., "Nitrate and Nitrite Removal from Raw and Ground Waters by Anion Exchange - A Review" Presented at the 67th Annual AIChE Meeting in Washington, D.C., August, 1974.
108. Sanks, R.L., and W.J. Kaufman, "Partial Demineralization of Brackish Waters," National Symposium on Sanitary Engineering Research, Design and Development, Penn. State Univ., University Park, PA., 1965.
109. Schmidt, K.D., "Nitrates and Groundwater Management in the Fresno Urban Area," J.AWWA, p. 146, March (1974).
110. Smith, G.E., "Nitrate Pollution of Water Supplies," Univ. of Missouri, Proceedings of 3rd. Annual Conf. on Trace Substances in Environmental Health 1969, pp. 273-287, (1970).
111. Smith, T.G. and J.S. Dranoff, "Film Diffusion-Controlled Kinetics in Binary Ion-Exchange", Ind. & Eng. Chem. Fundamentals, Vol. 3, No. 3., p. 195, 1964.
112. Snoeyink, V.L., and W.J. Weber, Jr., "Adsorption of Strong Acids, Phenol and 4-Nitrophenol by Active Carbon in Agitated Non-Flow Systems," Dept. of Civil Eng. Report T-68-3, Univ. of Michigan, Ann Arbor, 1968.
113. Soldano, B.A. and G.E. Boyd, "Self-Diffusion of Anions in Strong Base Anion Exchangers," J. ACS, V. 75, No. 24, p. 6099, Jan., 1954.
114. St. Amant, P.P. and P.L. McCarty, "Treatment of High Nitrate Waters," J. AWWA, Vol. 61, No. 12, p. 659, Dec., 1969.
115. St. Amant, P.P., L.A. Beck, "Nitrate Removal from Agricultural Wastewater" in Water Quality Management Problems in Arid Regions, J.P. Law et.al. Eds., NTIS No. PB 198 125, U.S. Dept. of Commerce, Springfield, Va., Oct., 1970.

116. Summers, W.K., and Z., Spiegel, Ground Water Pollution: a Bibliography, Ann Arbor Science, Ann Arbor, Mich., 1974.
117. Thompson, G.L., "Ground Water Resources of Nararro County, Texas," Texas Water Development Board, Rept. 160, 63 pp. (1972).
118. Todd, D.K., The Water Encyclopedia, Water Information Center, Port Washington, N.Y., 1970.
119. Tondeur D., and G. Klein, "Multicomponent Ion-Exchange in Fixed Beds" I&EC Fund., V. 6, No. 3, p. 351, August (1967).
120. Turner, J.C.R. and C.B. Snowdon, "Liquid-Side Mass-Transfer Coefficients in Ion Exchange: an Examination of the Nernst-Planck Model", Chem. Eng. Sci., V. 23, p. 221, 1968.
121. Turner, J.C.R. and C.B. Snowdon, "Liquid-Side Mass Transfer Coefficients in Ion-Exchange - the $H^+/Cu^{++}-Cl^-$ System" Chem. Eng. Sci., V. 23, p. 1099, 1968.
122. Univ. of California, Sanitary Engineering, Research Laboratory Staff, "Optimization of Ammonia Removal by Ion Exchange Using Clinoptilolite," Water Pollution Control Research Series Report No. 17080 DAR 09/71, U.S. GPO 1971.
123. University of Illinois, College of Engineering, "Proceedings of the 12th Sanitary Engineering Conference: Nitrate and Water Supply: Source and Control," Dept. of Civil Eng., Univ. of Ill., Urbana, Ill., Feb. (1970).
124. Univ. of Michigan Statistical Research Lab Staff, A Manual of Elementary Statistics Using MIDAS, First Ed., Statistical Research Laboratory, The University of Michigan, Ann Arbor, 1975.
125. U.S. Dept. of Health, Education and Welfare, "Public Health Service Drinking Water Standards," Public Health Service Publication No. 956, U.S. GPO, Washington, D.C., 1962.
126. U.S. Environmental Protection Agency, Manual on Methods of Chemical Analysis of Water and Wastes, U.S. EPA Office of Technology Transfer, Washington, D.C. 20460, 1974.

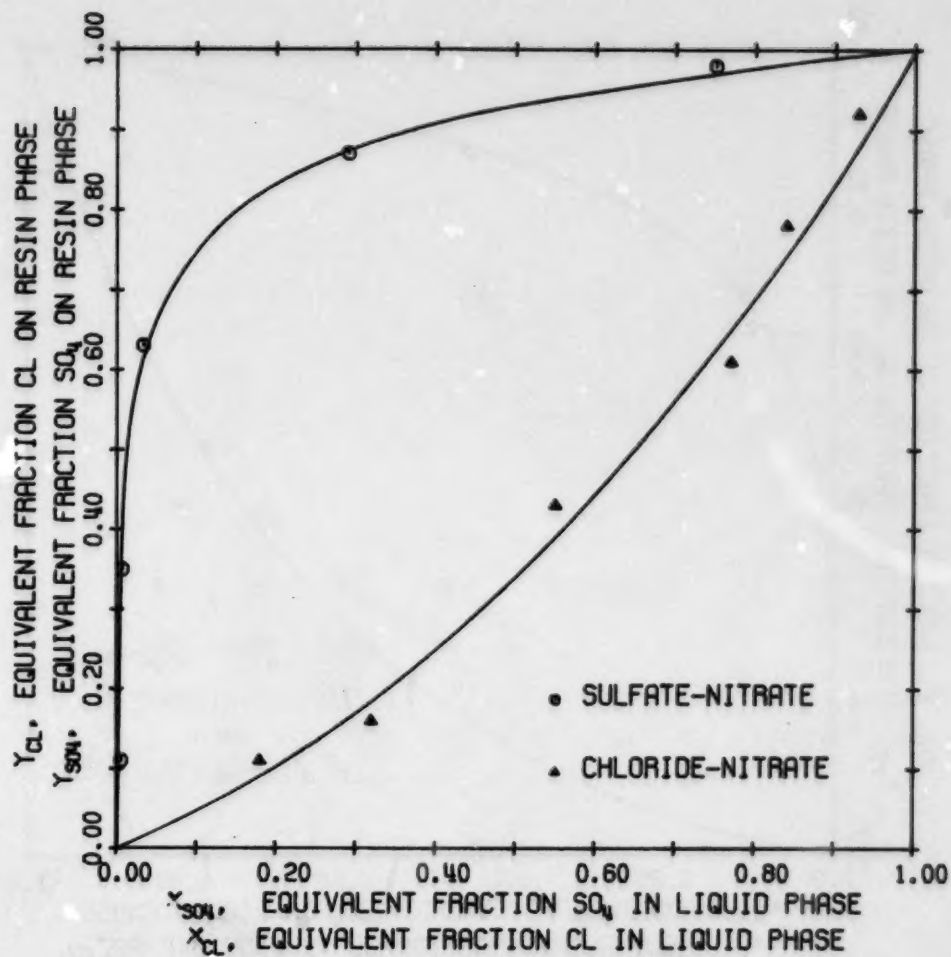
127. U.S. EPA, "Interim Primary Drinking Water Standards," Federal Register, December 24, 1975.
128. Van Brocklin, L.P., "Ionic Migration Effects on Liquid-Resistance - Controlled Ion Exchange" Ph.D. Thesis, University of Washington, 1968.
129. Walitt, A.L. and H.L. Jones, "Basic Salinogen Ion-Exchange Resins for Selective Nitrate Removal from Potable and Effluent Waters," U.S. EPA, Cincinnati, Advanced Waste Treatment Laboratory, 1970, U.S. GPO, Washington, D.C.
130. Walker, E.H., "Ground Water Resources of the Hopkinville Quadrangle, Kentucky," USGS WSP 1328, (1956).
131. Ward, Paul C., "Existing Levels of Nitrates in Waters-the California Situations," 12th Annual Sanitary Eng. Conf., Univ. of Ill., Urbana, Ill., Feb., 1970.
132. Weber, O.W., I.F. Miller and H.P. Gregor, "The Adsorption of Carbon Dioxide by Weak Base Ion-Exchange Resins," A.I.Ch.E.J., V. 16, No. 4, p. 609, 1970.
133. Weber, W.J., Jr., Physiochemical Processes for Water Quality Control, Wiley Interscience, New York, 1972.
134. Weiss, D.E., et.al., "Thermally Regenerated Ion-Exchange Process: an Aid to Water Management" J. WPCF, V. 38, p. 1782, 1966.
135. Weiss, D.E., B.A. Bolto, R. McNeill, A.S. MacPherson, R. Siudak, E.A. Swinton, and D. Willis, "An Ion-Exchange Process With Thermal Regeneration II. Properties of Weakly Basic Ion-Exchange Resins." Australian J. Chem., V. 19, p. 561, 1966.
136. Wilkander, L., Ann. Royal Agr. Coll. Sweden, V. 14, p. 1-171 (1956).

APPENDIX A



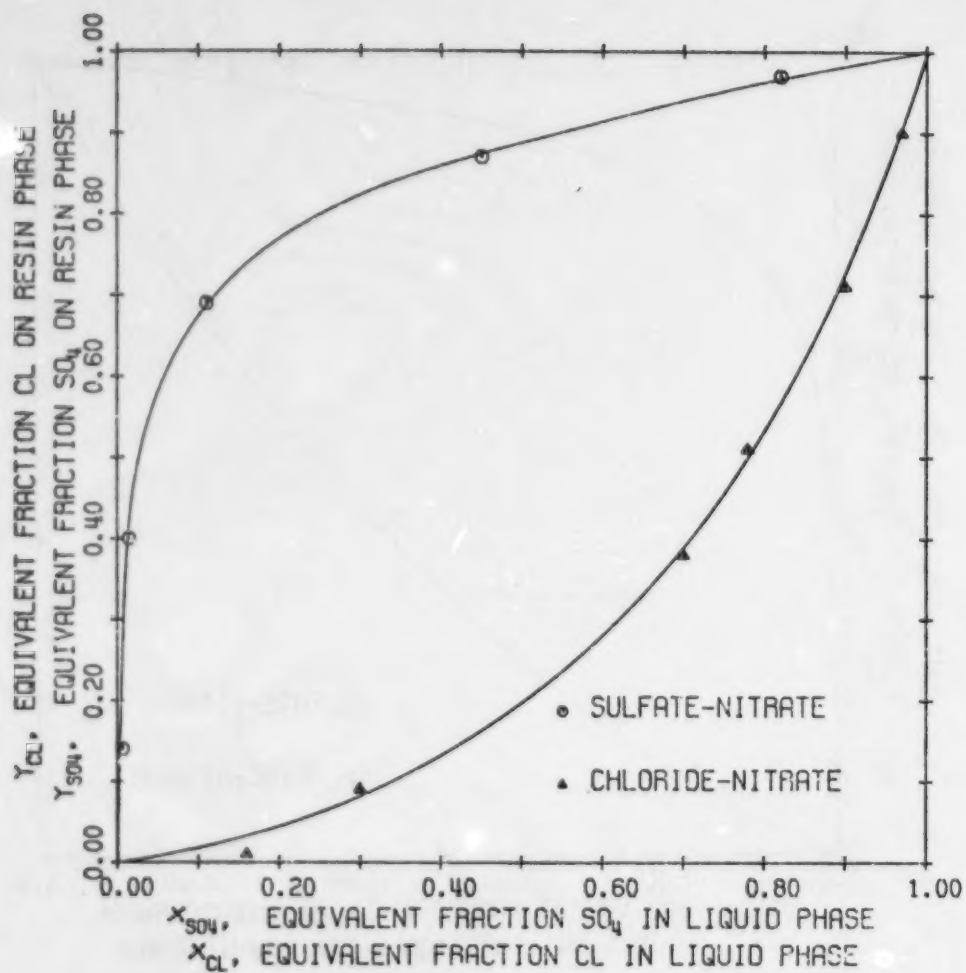
RESIN NUMBER 1
AMBERLITE IRA 93, MACROPOROUS RESIN
STYRENE-DVB MATRIX
TERTIARY-AMINE FUNCTIONALITY
TOTAL CAPACITY=1.25 MEQ/ML

FIGURE A1
25° C, BINARY ION-EXCHANGE ISOTHERM



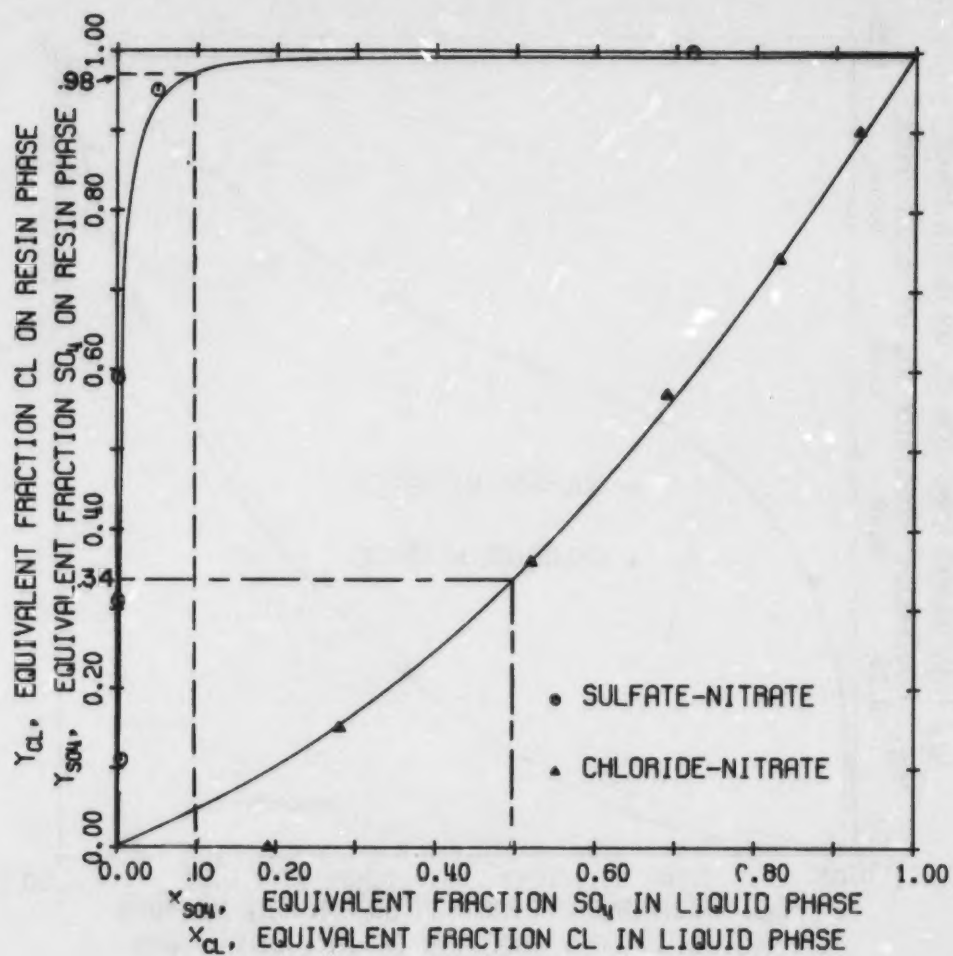
RESIN NUMBER 2
 AMBERLITE IRA 68, MICROPOROUS GEL
 POLYACRYLIC MATRIX
 TERTIARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.6 MEQ/ML

FIGURE A2
 25° C. BINARY ION-EXCHANGE ISOTHERM



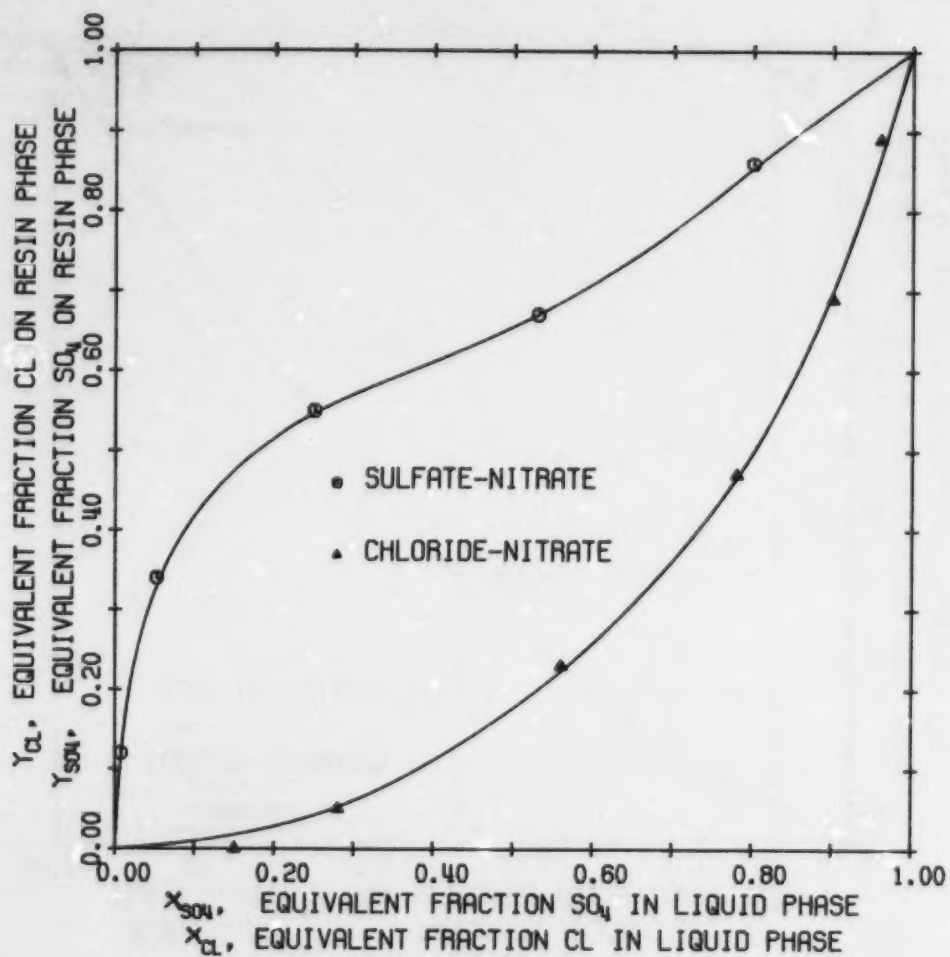
RESIN NUMBER 3
AMBERLITE IR 45, MICROPOROUS GEL
STYRENE-DVB MATRIX
POLYAMINE FUNCTIONALITY
TOTAL CAPACITY=1.9 MEQ/ML

FIGURE A3
25° C, BINARY ION-EXCHANGE ISOTHERM



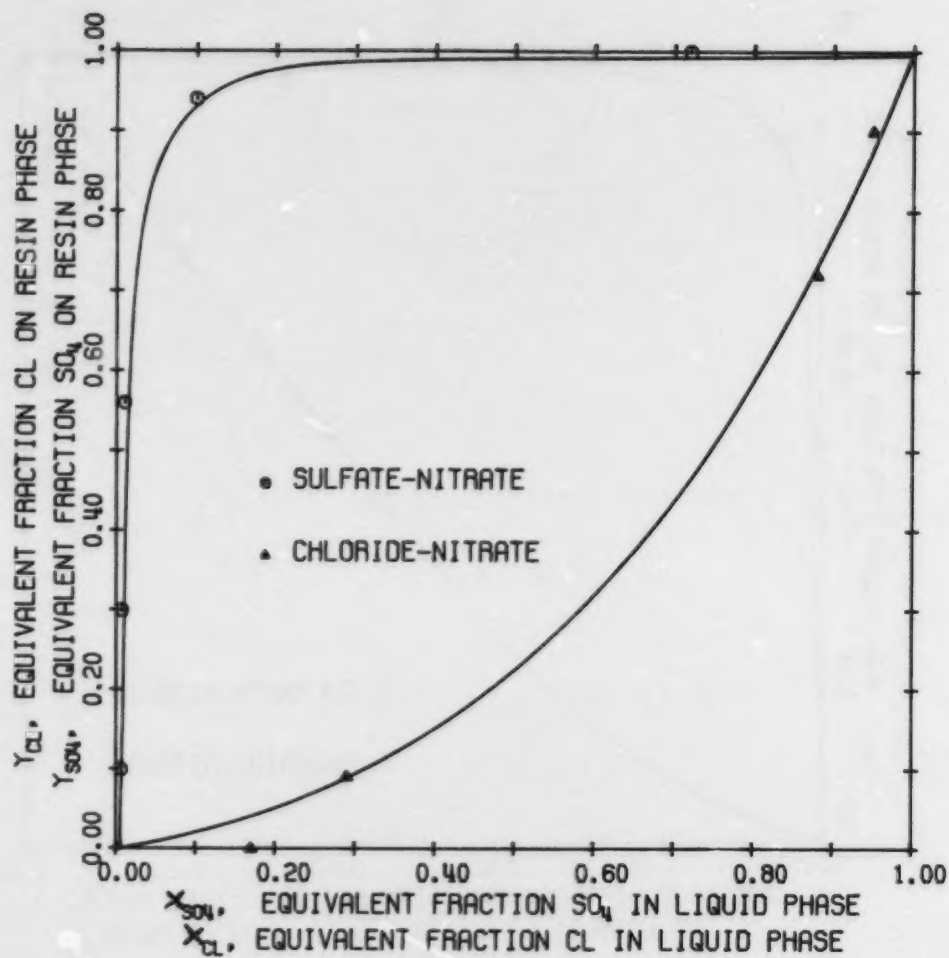
RESIN NUMBER 4
 DOWEX WGR, MICROPOROUS GEL
 EPOXY-AMINE MATRIX
 POLYAMINE FUNCTIONALITY
 TOTAL CAPACITY=1.0 MEQ/ML

FIGURE A4
 25° C, BINARY ION-EXCHANGE ISOTHERM



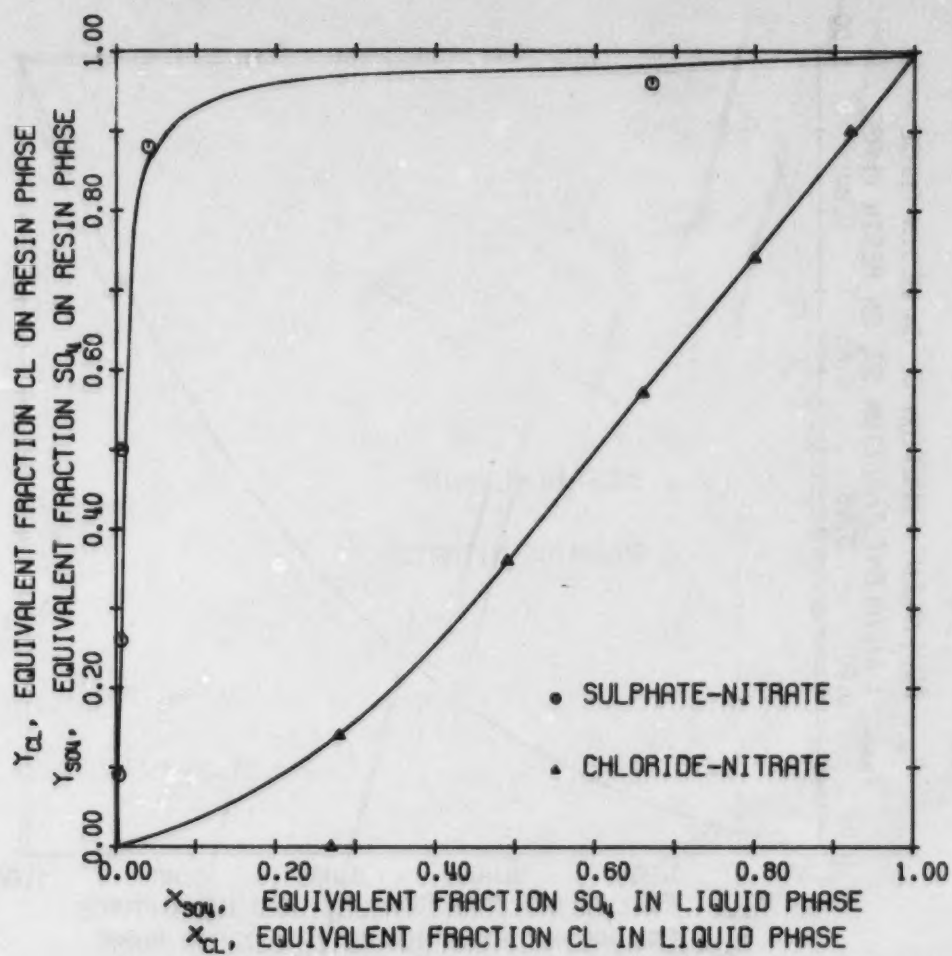
RESIN NUMBER 5
DOWEX MWA-1, MACROPOROUS RESIN
STYRENE-DVB MATRIX
TERTIARY-AMINE FUNCTIONALITY
TOTAL CAPACITY=1.1 MEQ/ML

FIGURE A5
25° C, BINARY ION-EXCHANGE ISOTHERM



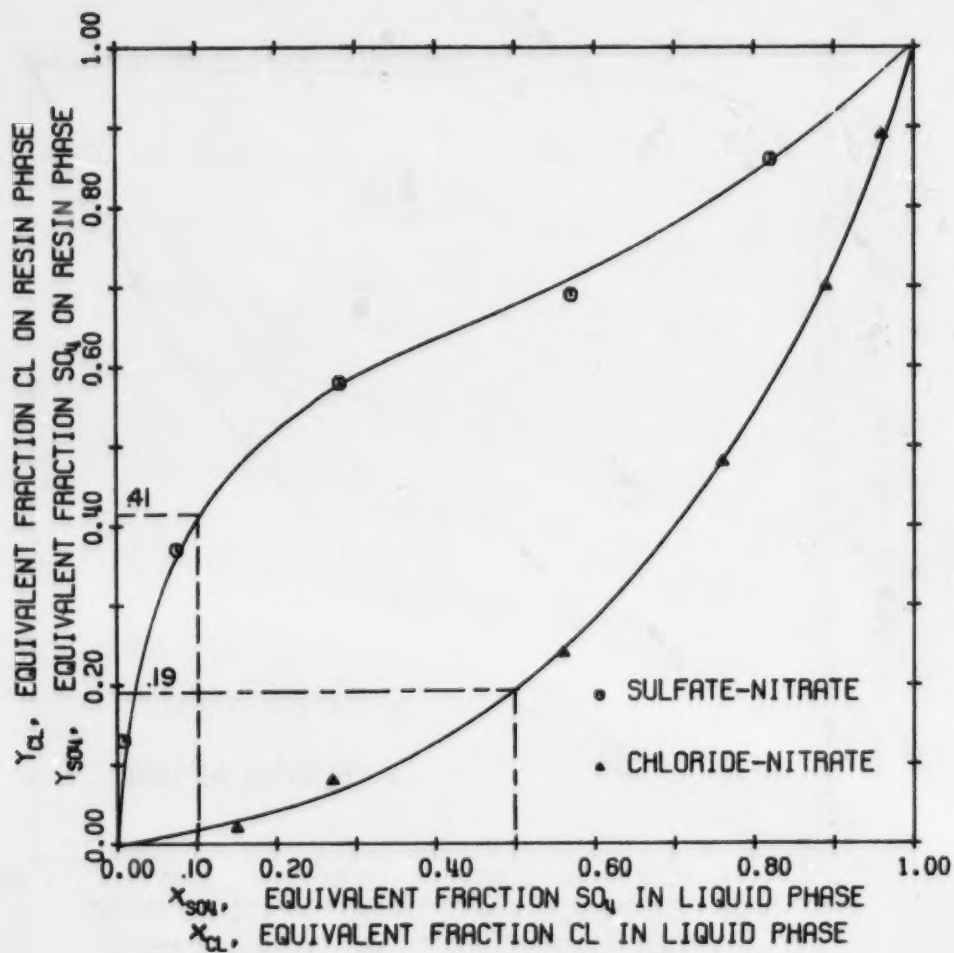
RESIN NUMBER 6
DUOLITE A-7, MACROPOROUS GRANULAR RESIN
PHENOL-FORMALDEHYDE MATRIX
SECONDARY-AMINE FUNCTIONALITY
(POLYAMINE TITRATION CURVE)
TOTAL CAPACITY=2.4 MEQ/ML

FIGURE AG
25° C, BINARY ION-EXCHANGE ISOTHERM



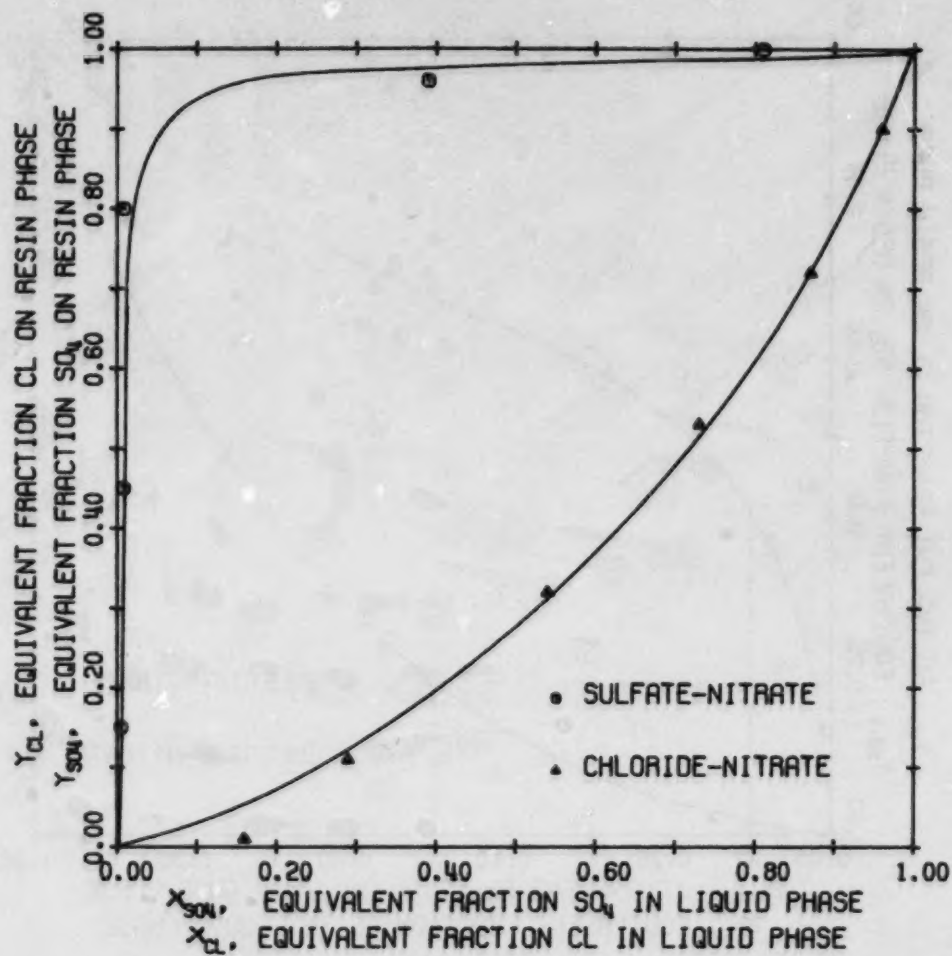
RESIN NUMBER 7
DUOLITE A 340, MICROPOROUS GEL
EPOXY-AMINE MATRIX
POLYAMINE FUNCTIONALITY
TOTAL CAPACITY=2.6 MEQ/ML

FIGURE A7
25° C, BINARY ION-EXCHANGE ISOTHERM



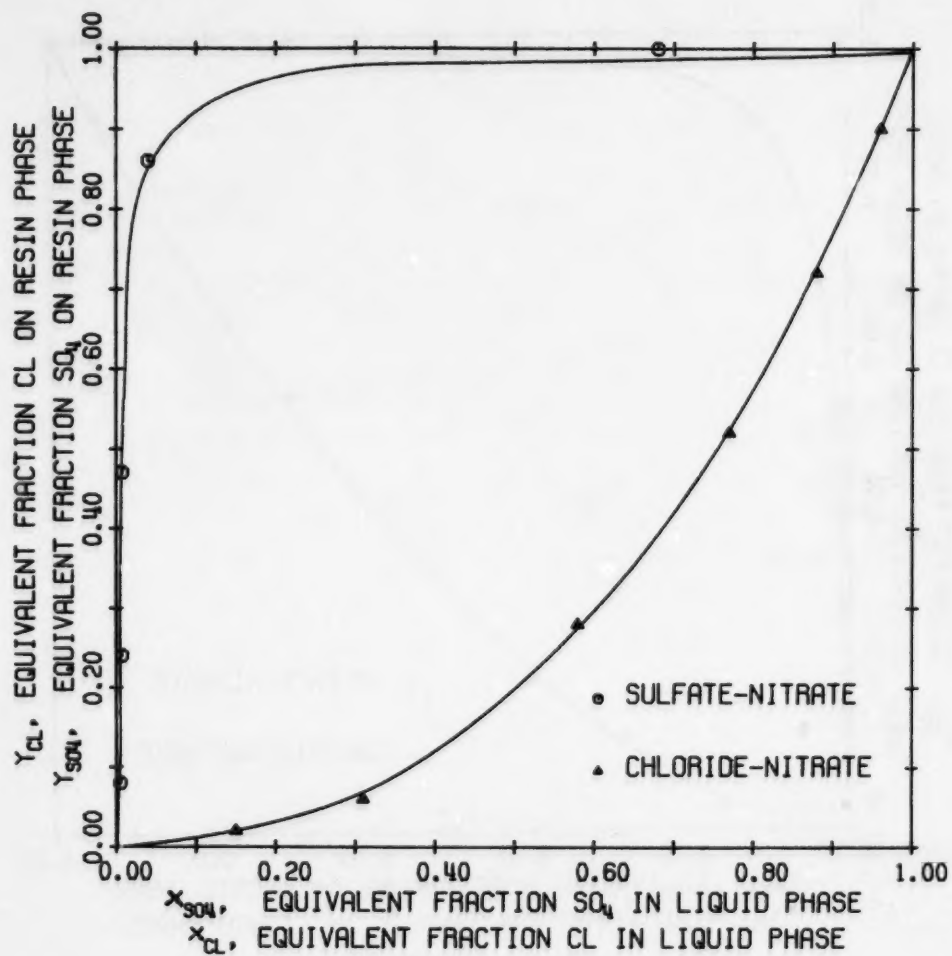
RESIN NUMBER 8
 DUOLITE ES 368, MACROPOROUS RESIN
 STYRENE-DVB MATRIX
 TERTIARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.3 MEQ/ML

FIGURE A8
 25° C, BINARY ION-EXCHANGE ISOTHERM



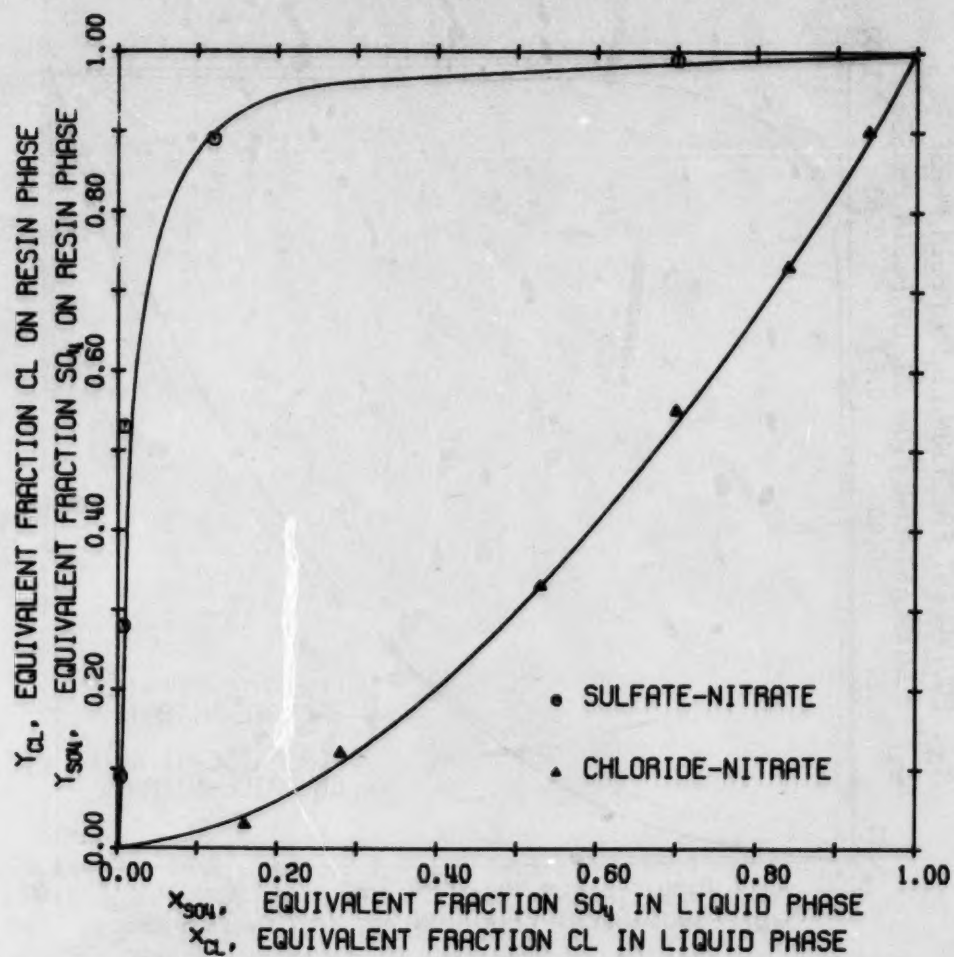
RESIN NUMBER 9
DUOLITE ES 561, MACROPOROUS GRANULAR RESIN
PHENOL-FORMALDEHYDE MATRIX
POLYAMINE FUNCTIONALITY
TOTAL CAPACITY=2.0 MEQ/ML

FIGURE A9
25° C, BINARY ION-EXCHANGE ISOTHERM



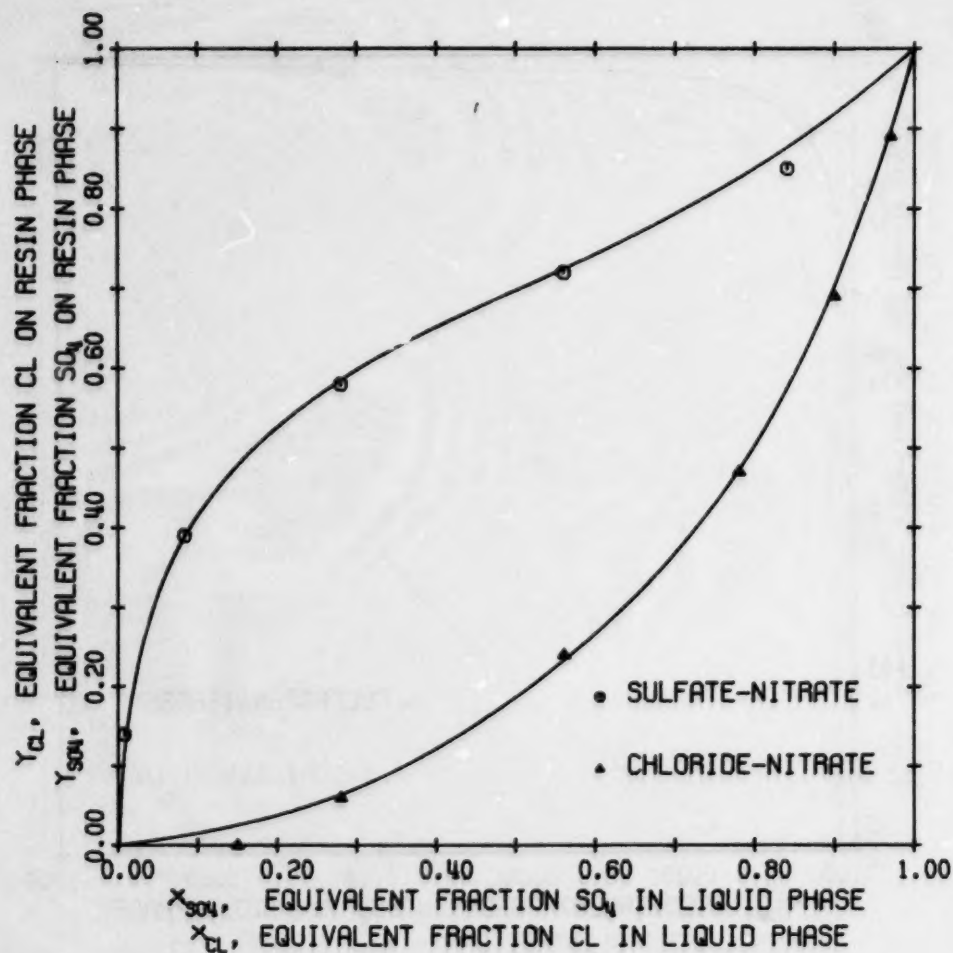
RESIN NUMBER 10
DUOLITE ES 374, MACROPOROUS RESIN
POLYACRYLIC MATRIX
TERTIARY-AMINE FUNCTIONALITY
(POLYAMINE TITRATION CURVE)
TOTAL CAPACITY=3.0 MEQ/ML

FIGURE A10
25° C, BINARY ION-EXCHANGE ISOTHERM



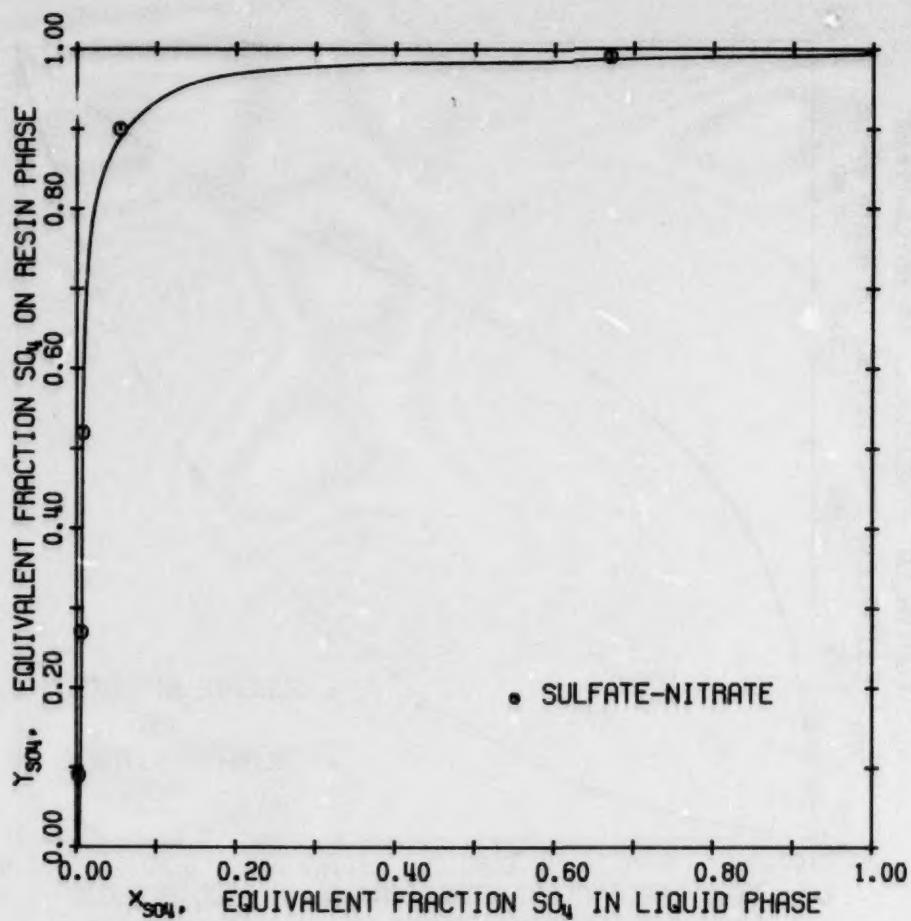
RESIN NUMBER 11
 IONIC A-260, MICROPOROUS GRANULAR GEL
 ALIPHATIC-AMINE MATRIX
 POLYAMINE FUNCTIONALITY
 TOTAL CAPACITY=1.8 MEQ/ML

FIGURE A11
 25° C, BINARY ION-EXCHANGE ISOTHERM



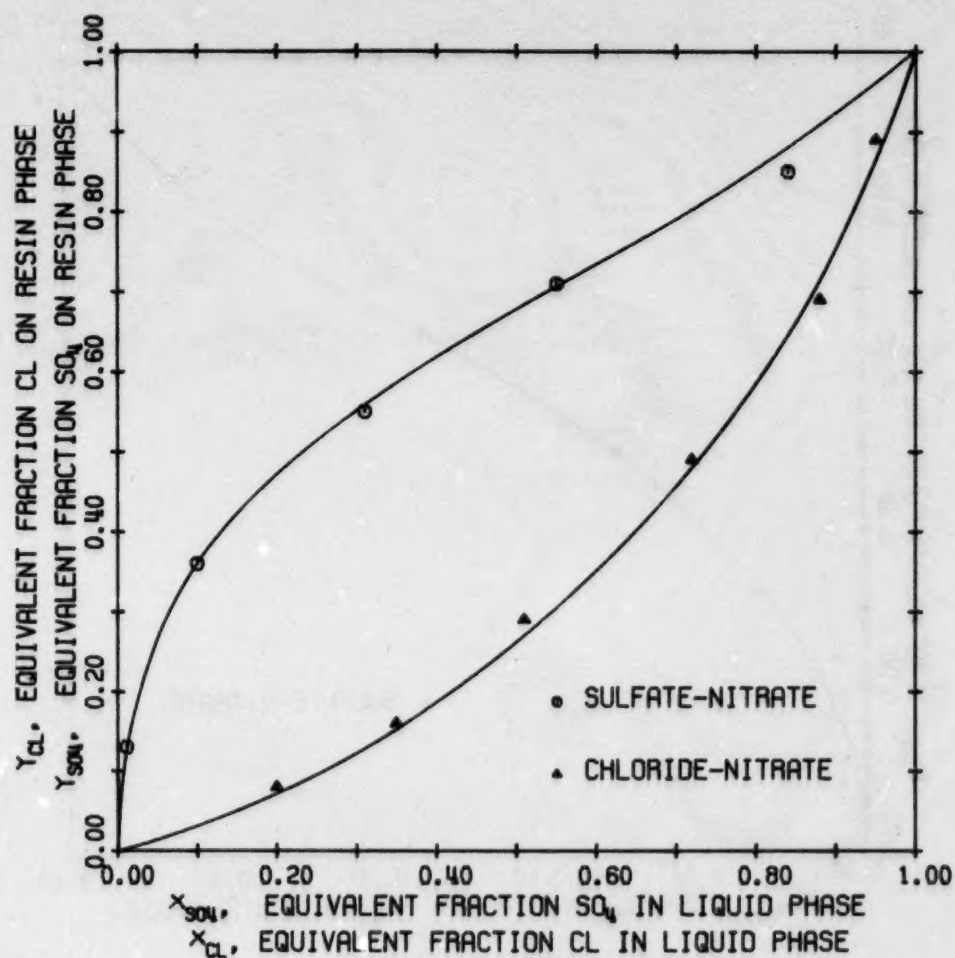
RESIN NUMBER 12
IONAC AFP 329, MACROPOROUS RESIN
STYRENE-DVB MATRIX
TERTIARY-AMINE FUNCTIONALITY
TOTAL CAPACITY=1.25 MEQ/ML

FIGURE A12
25° C, BINARY ION-EXCHANGE ISOTHERM



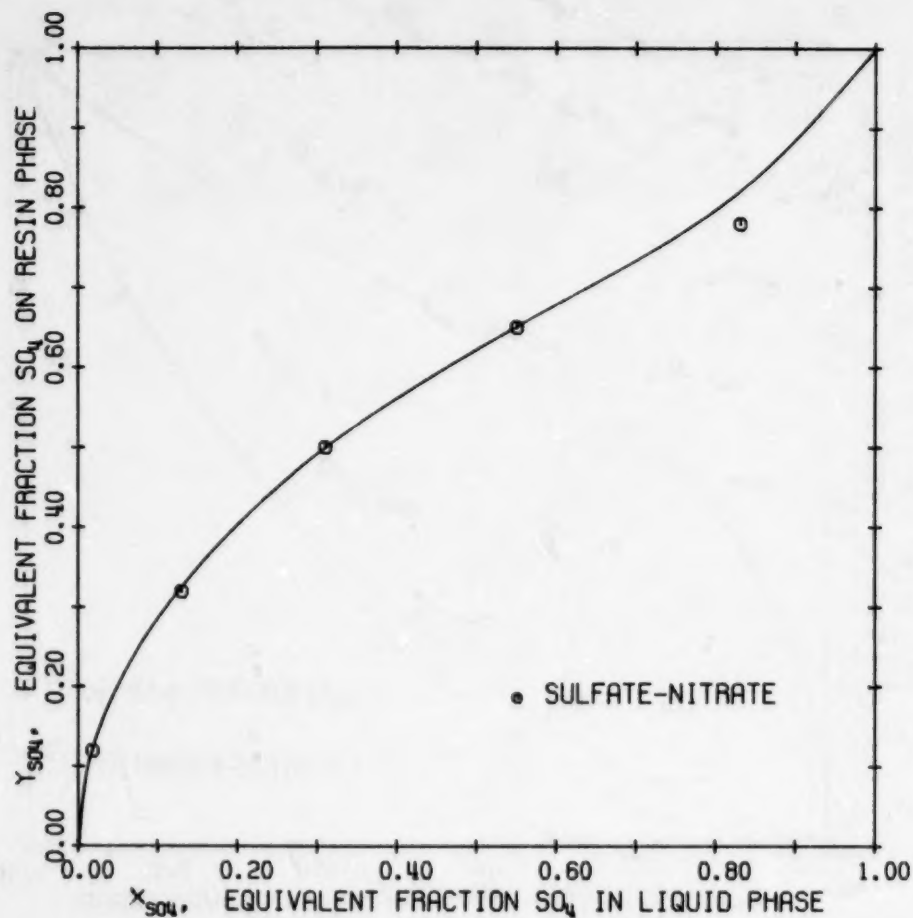
RESIN NUMBER 13
 IONAC A-305, MICROPOROUS GRANULAR GEL
 EPOXY-AMINE MATRIX
 POLYAMINE FUNCTIONALITY (INCL. QUAT. AMINE)
 TOTAL CAPACITY=3.5 MEQ/ML

FIGURE A13
 25° C, BINARY ION-EXCHANGE ISOTHERM



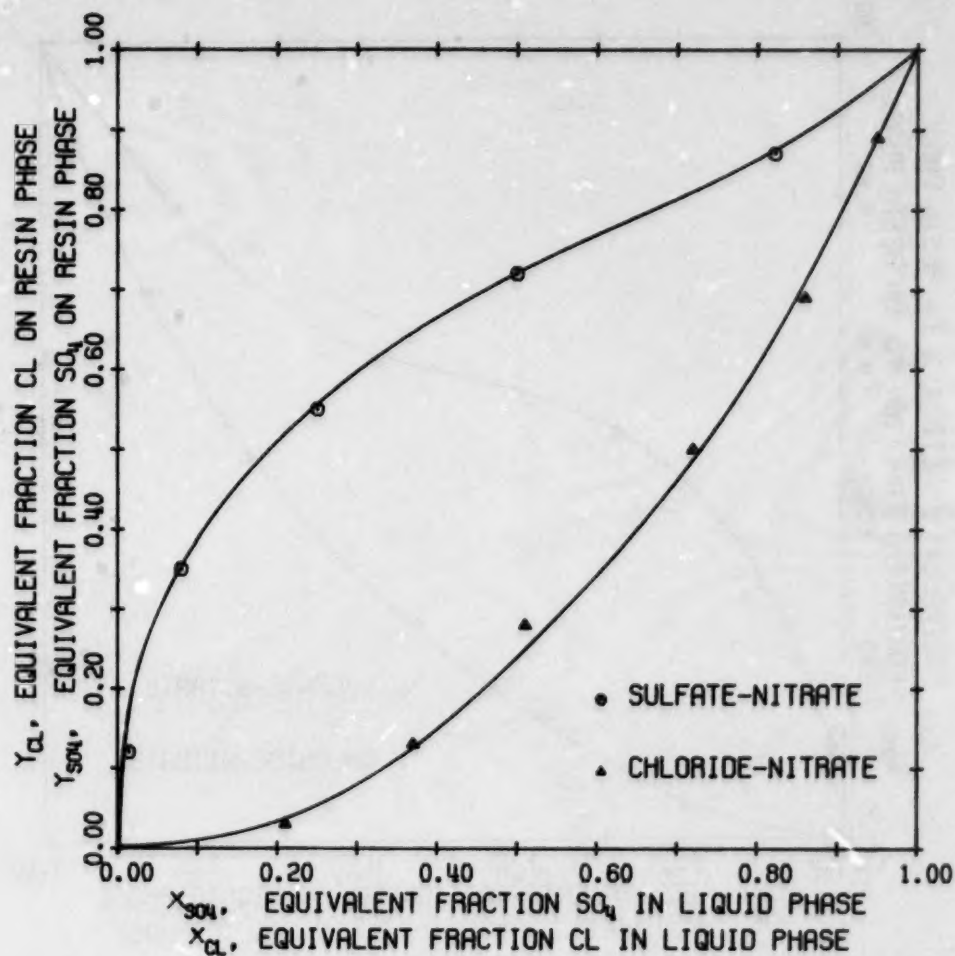
RESIN NUMBER 14
 AMBERLITE IRA 910, MACROPOROUS RESIN
 STYRENE-DVB MATRIX
 TYPE II, QUATERNARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.0 MEQ/ML

FIGURE A14
 25° C, BINARY ION-EXCHANGE ISOTHERM



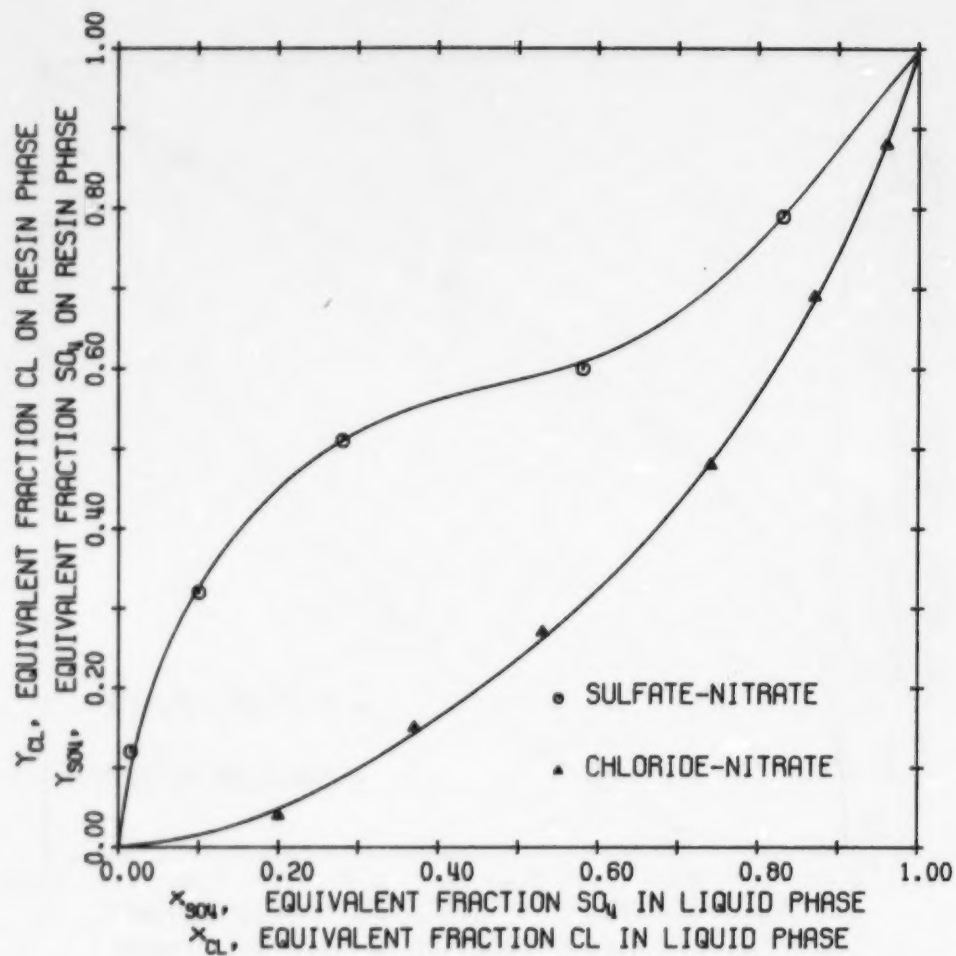
RESIN NUMBER 15
 AMBERLITE IRA 400, MICROPOROUS GEL
 STYRENE-DVB MATRIX
 TYPE I, QUATERNARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.4 MEQ/ML

FIGURE A15
 25° C, BINARY ION-EXCHANGE ISOTHERM



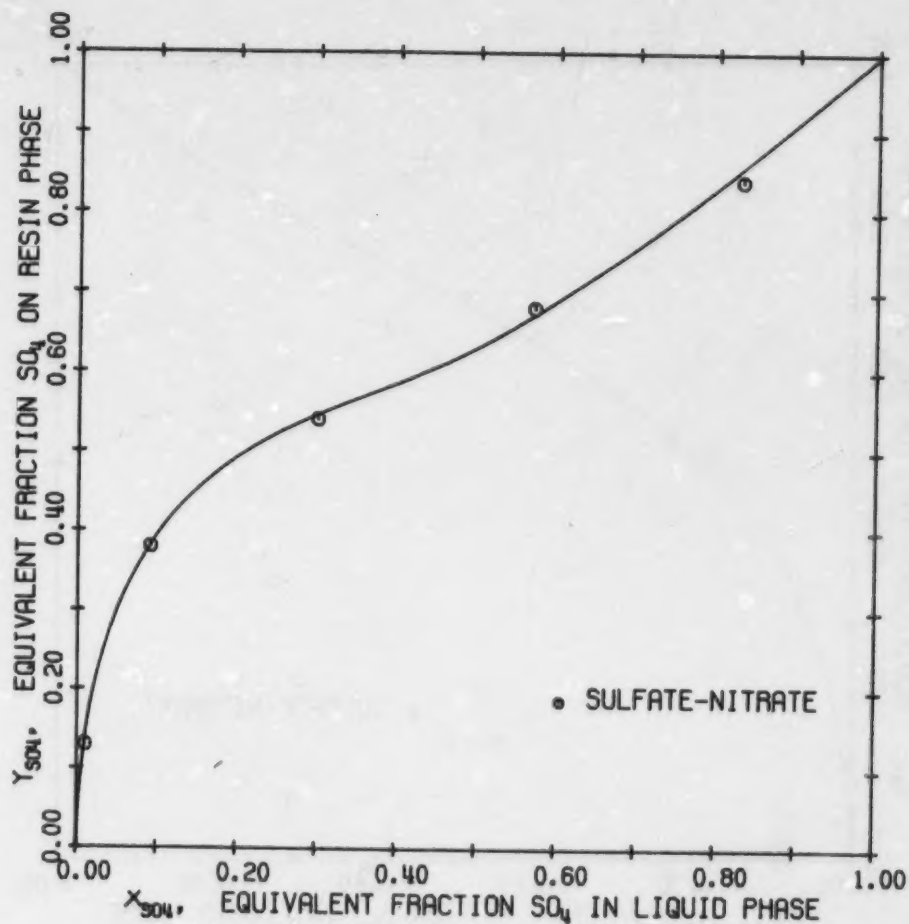
RESIN NUMBER 16
 AMBERLITE IRA 402, "IMPROVED" POROSITY RESIN
 STYRENE-DVB MATRIX
 TYPE I, QUATERNARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.25 MEQ/ML

FIGURE A16
 25° C, BINARY ION-EXCHANGE ISOTHERM



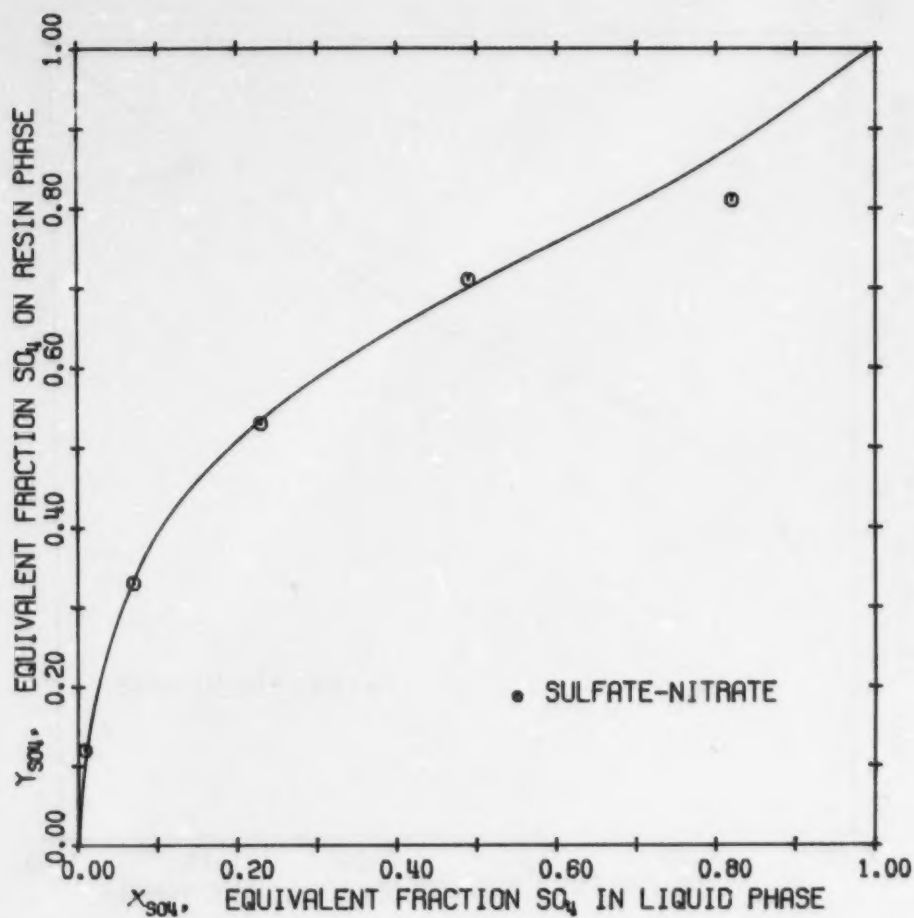
RESIN NUMBER 17
 AMBERLITE IRA 900, MACROPOROUS RESIN
 STYRENE-DVB MATRIX
 TYPE I, QUATERNARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.0 MEQ/ML

FIGURE A17
 25° C, BINARY ION-EXCHANGE ISOTHERM



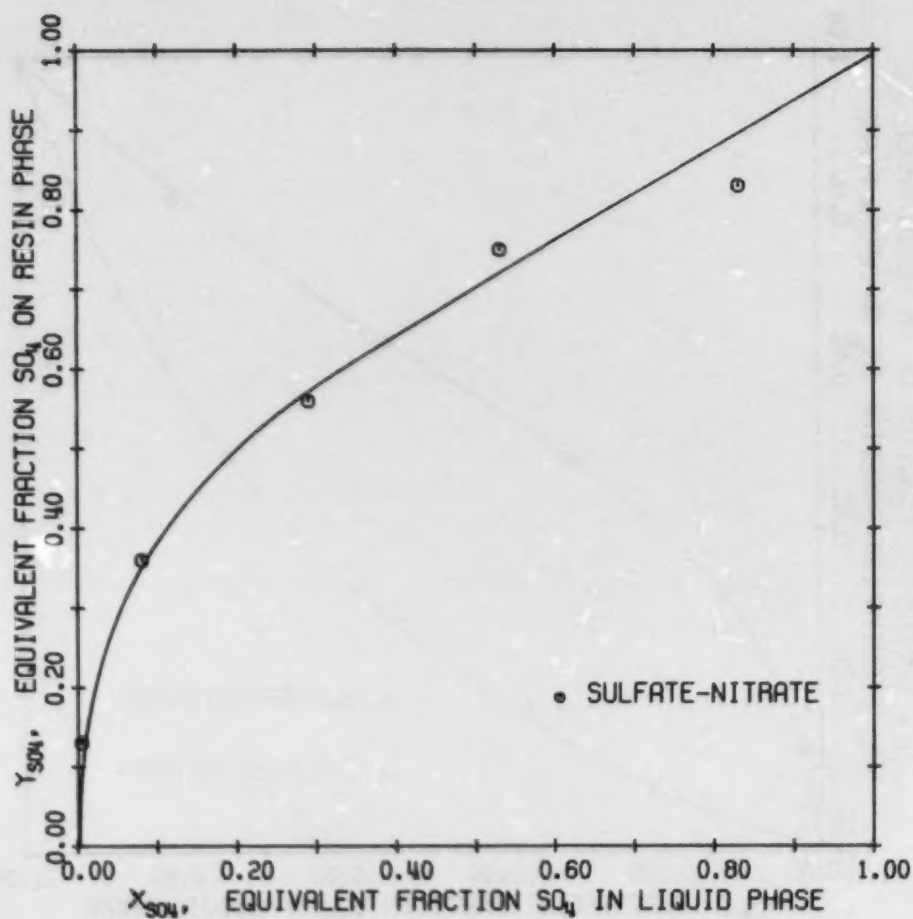
RESIN NUMBER 18
 AMBERLITE IRA 410, MICROPOROUS GEL
 STYRENE-DVB MATRIX
 TYPE II, QUATERNARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.35 MEQ/ML

FIGURE A18
 25° C, BINARY ION-EXCHANGE ISOTHERM



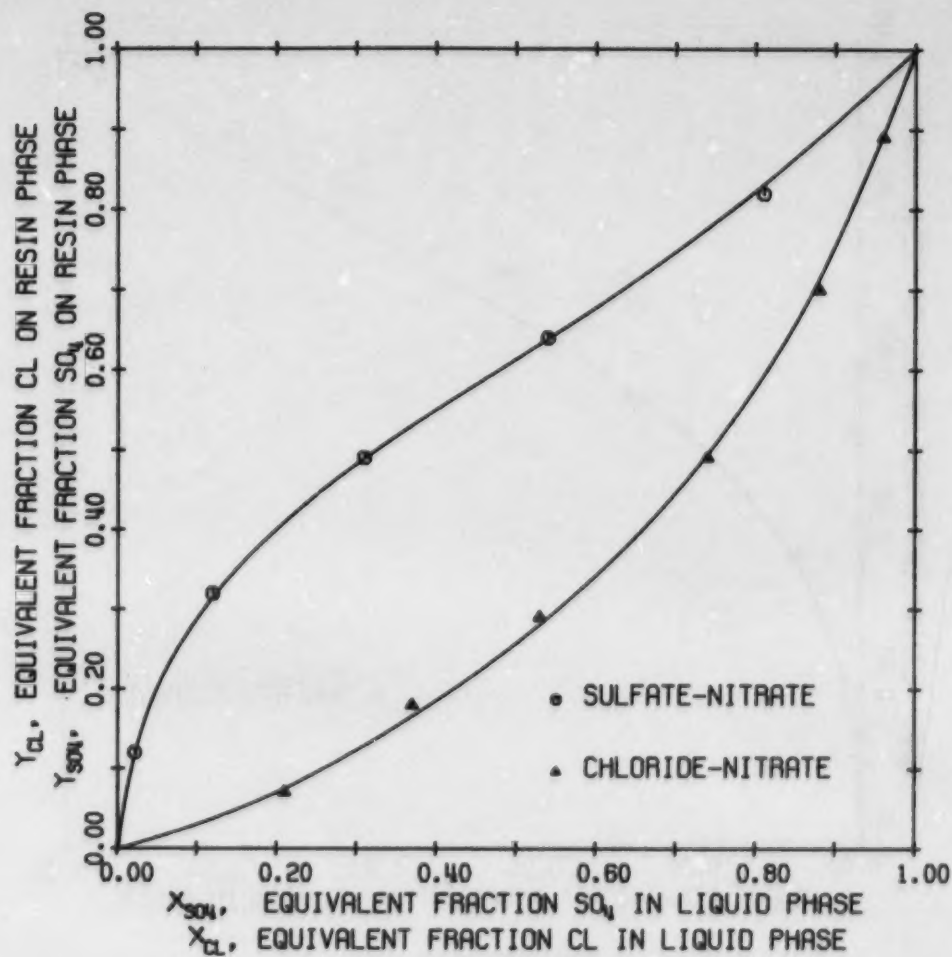
RESIN NUMBER 19
DOWEX SBR-P, "IMPROVED" POROSITY GEL
STYRENE-DVB MATRIX
TYPE I, QUATERNARY-AMINE FUNCTIONALITY
TOTAL CAPACITY=1.2 MEQ/ML

FIGURE A19
25° C, BINARY ION-EXCHANGE ISOTHERM



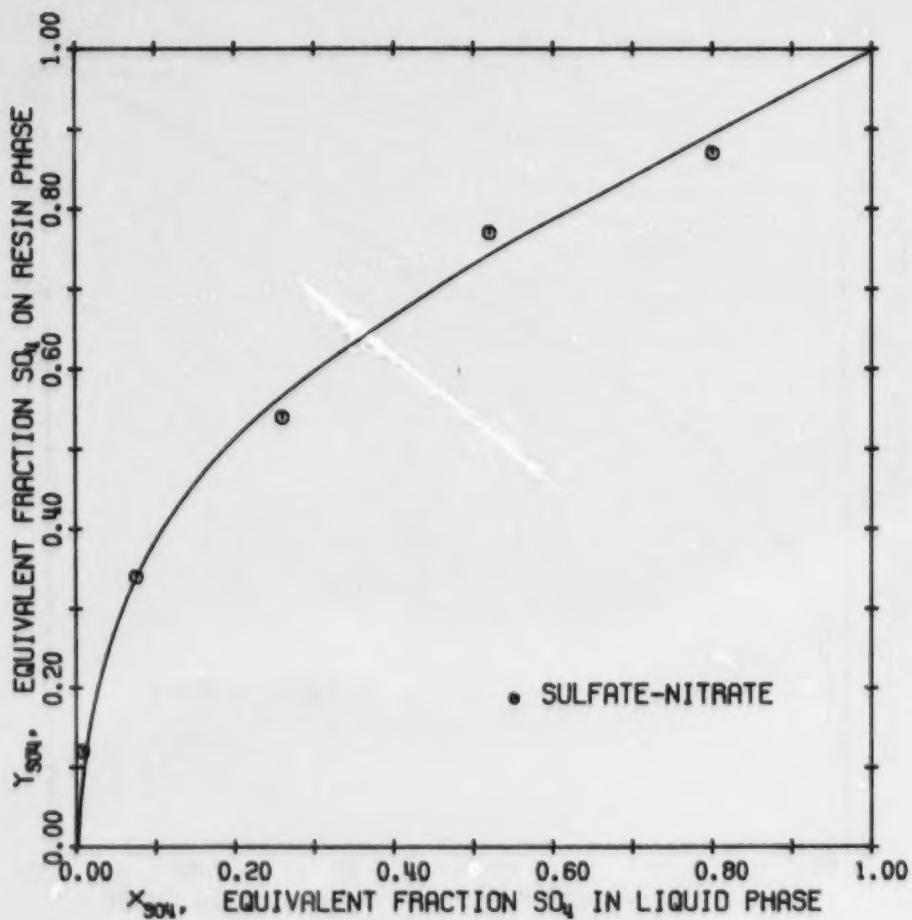
RESIN NUMBER 20
 DOWEX SAR, MICROPOROUS GEL
 STYRENE-DVB MATRIX
 TYPE II, QUATERNARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.4 MEQ/ML

FIGURE A20
 25° C, BINARY ION-EXCHANGE ISOTHERM



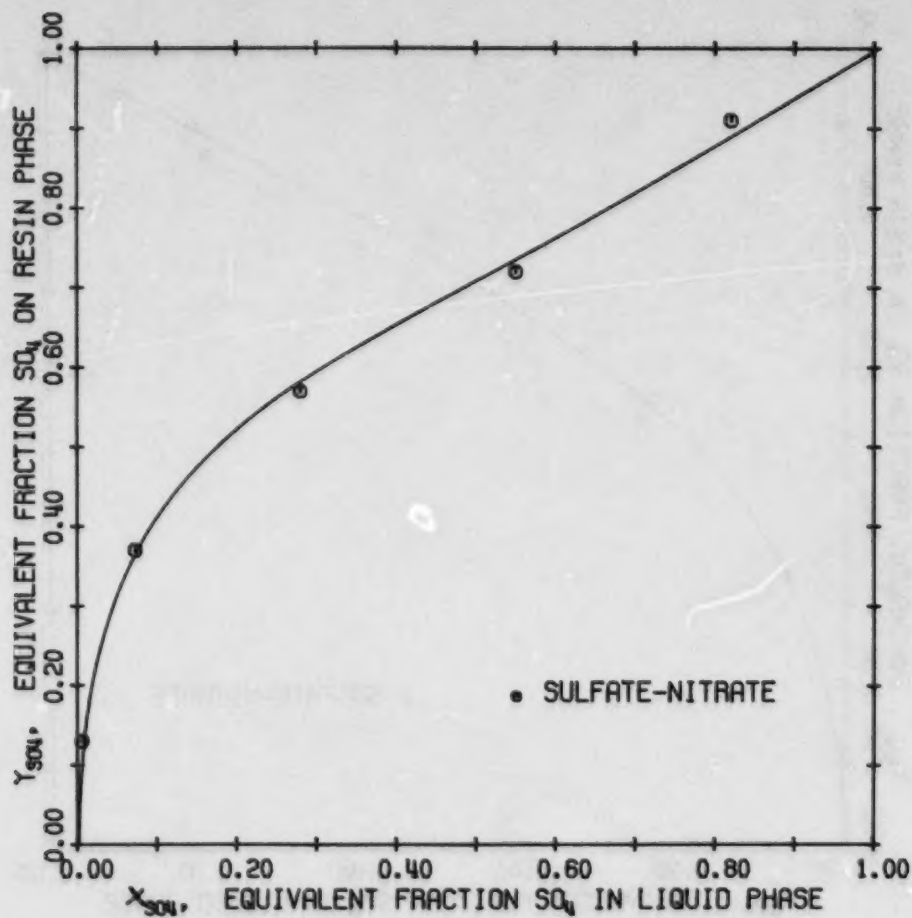
RESIN NUMBER 21
DOWEX SBA, MICROPOROUS GEL
STYRENE-DVB MATRIX
TYPE I, QUATERNARY-AMINE FUNCTIONALITY
TOTAL CAPACITY=1.4 MEQ/ML

FIGURE A21
25° C, BINARY ION-EXCHANGE ISOTHERM



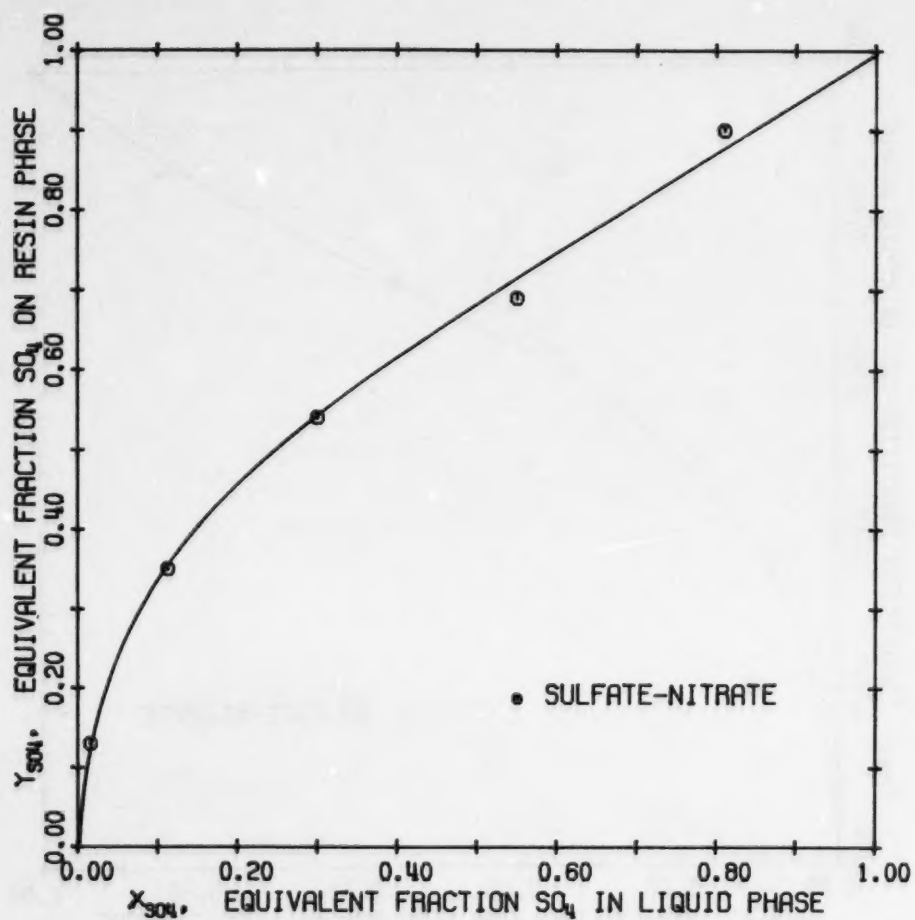
RESIN NUMBER 22
 DOWEX 11, "IMPROVED" POROSITY GEL
 STYRENE-DVB MATRIX
 TYPE I, QUATERNARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.2 MEQ/ML

FIGURE A22
 25° C, BINARY ION-EXCHANGE ISOTHERM



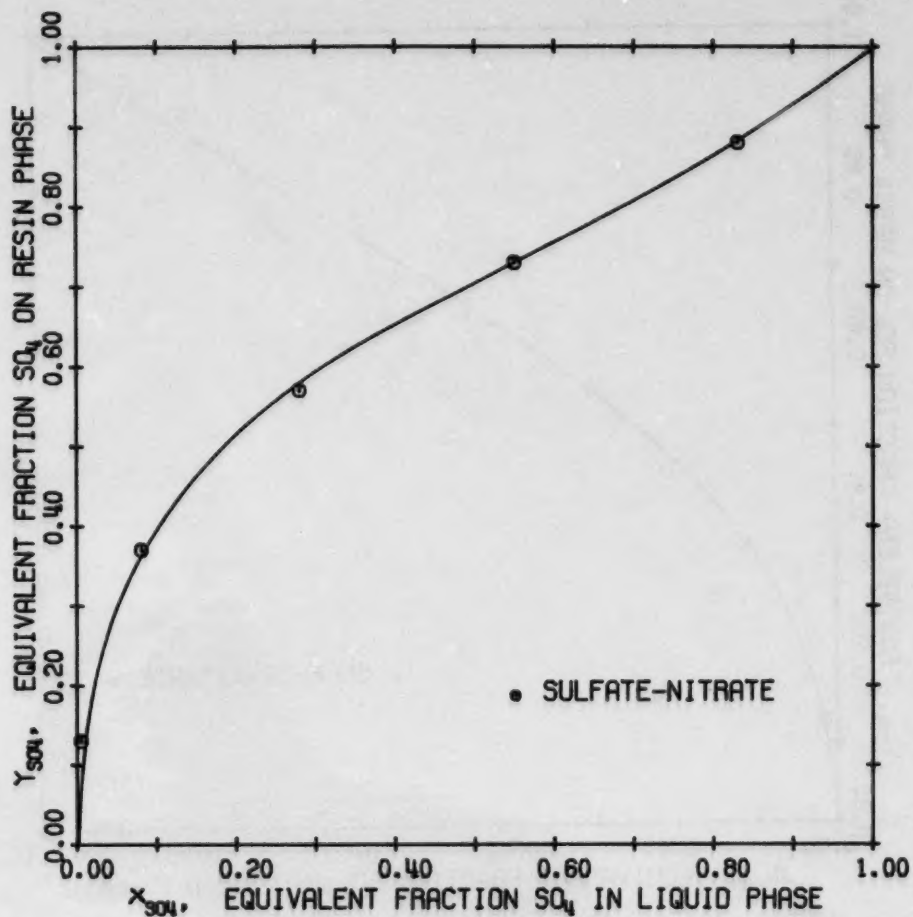
RESIN NUMBER 23
 DUOLITE A-102-D, MICROPOROUS GEL
 STYRENE-DVB MATRIX
 TYPE II, QUATERNARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.4 MEQ/ML

FIGURE A23
 25° C, BINARY ION-EXCHANGE ISOTHERM



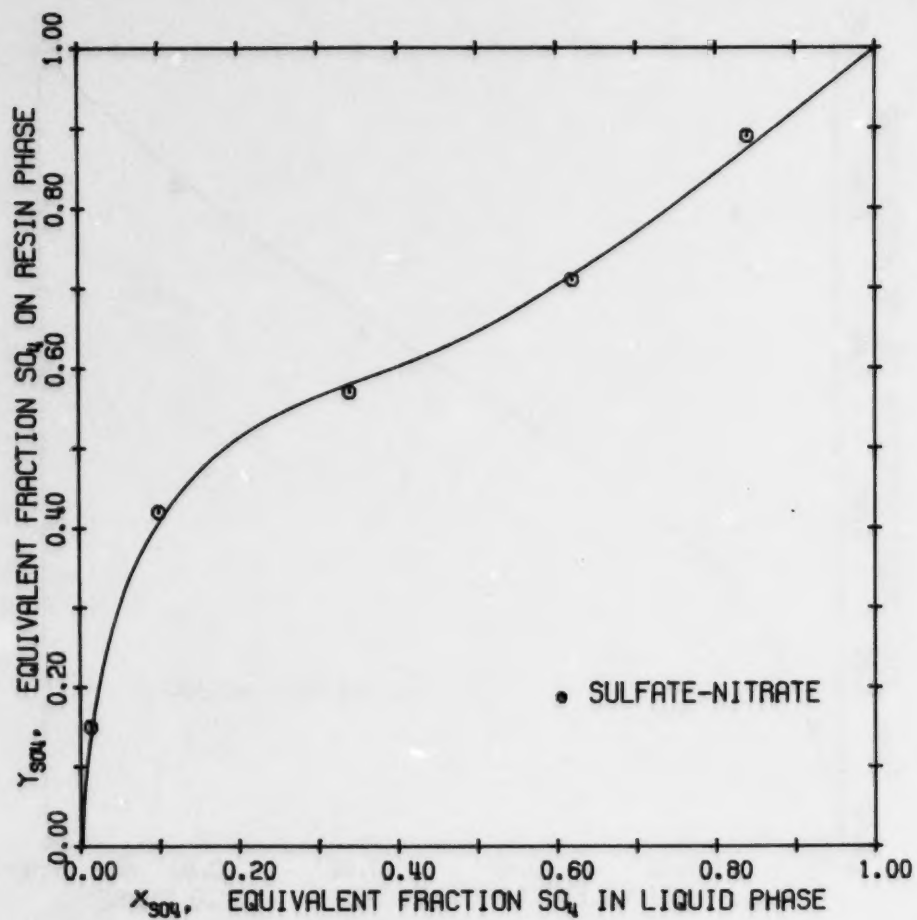
RESIN NUMBER 24
 DUOLITE A-101-D, "IMPROVED" POROSITY GEL
 STYRENE-DVB MATRIX
 TYPE I, QUATERNARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.3 MEQ/ML

FIGURE A24
 25° C, BINARY ION-EXCHANGE ISOTHERM



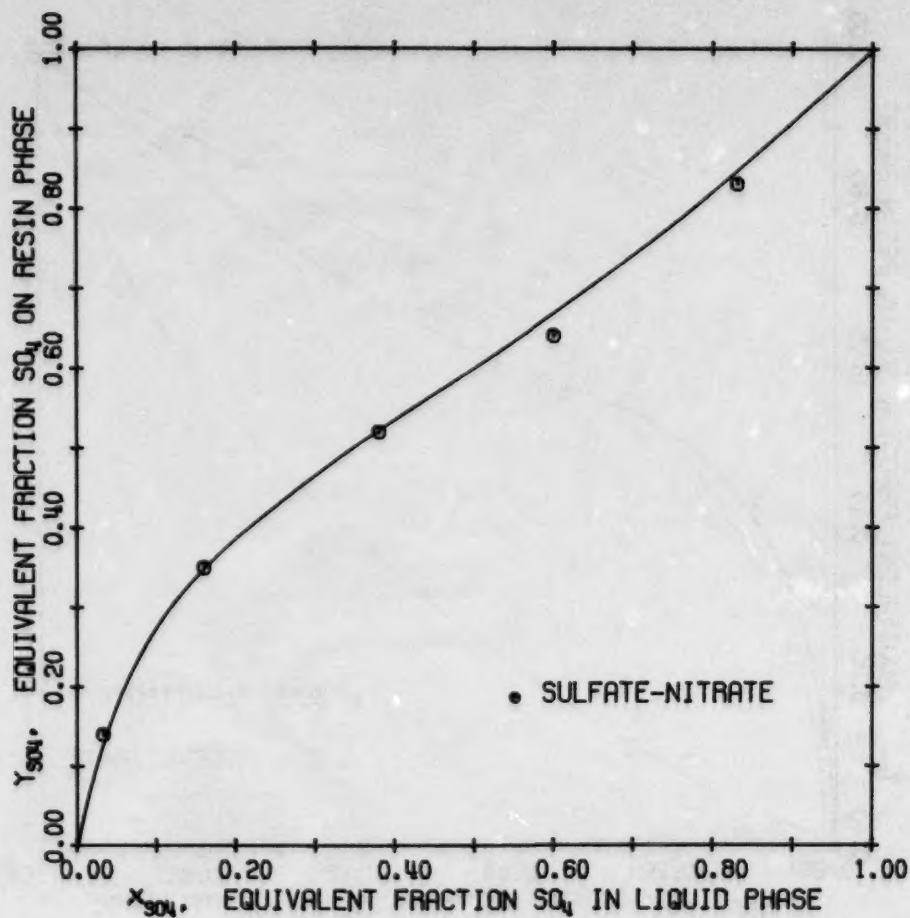
RESIN NUMBER 25
 DUOLITE A-104, MICROPOROUS GEL
 STYRENE-DVB MATRIX
 TYPES I & II QUATERNARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.5 MEQ/ML

FIGURE A25
 25° C, BINARY ION-EXCHANGE ISOTHERM



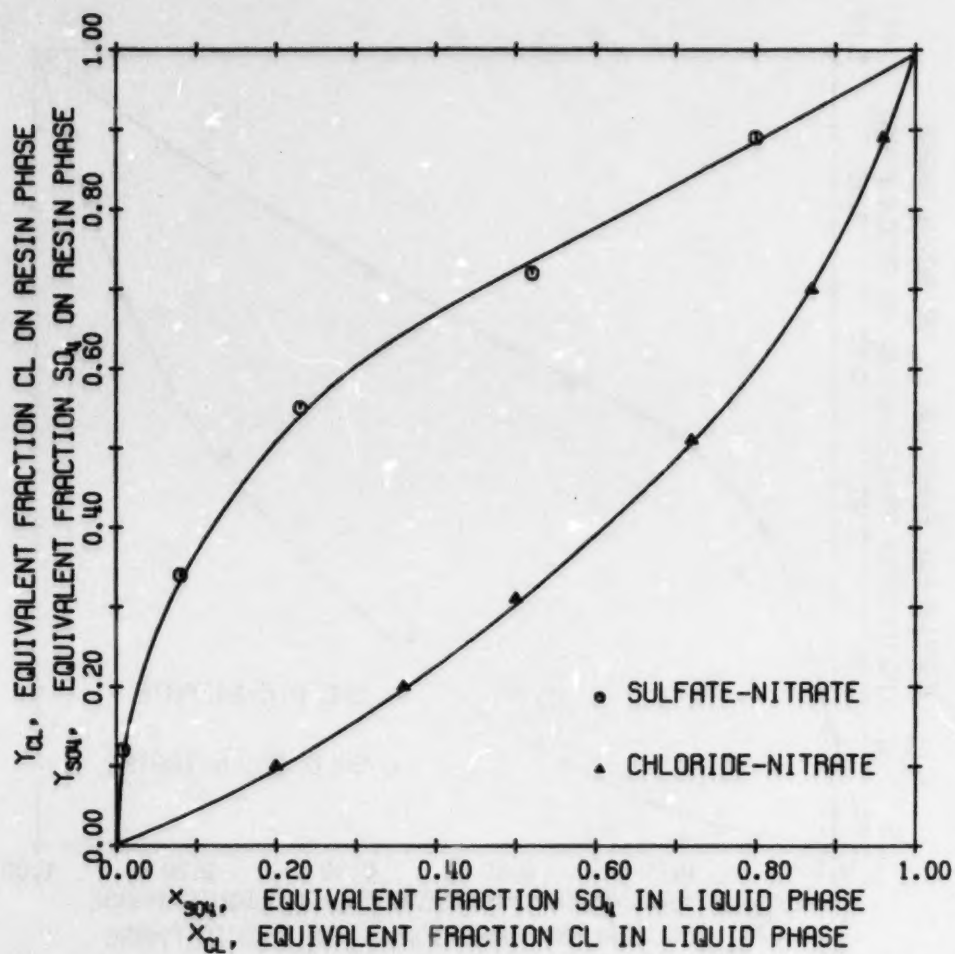
RESIN NUMBER 26
 IONAC A-550, "IMPROVED" POROSITY GEL
 POLYSTYRENE MATRIX
 TYPE II, QUATERNARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.3 MEQ/ML

FIGURE A26
 25° C, BINARY ION-EXCHANGE ISOTHERM



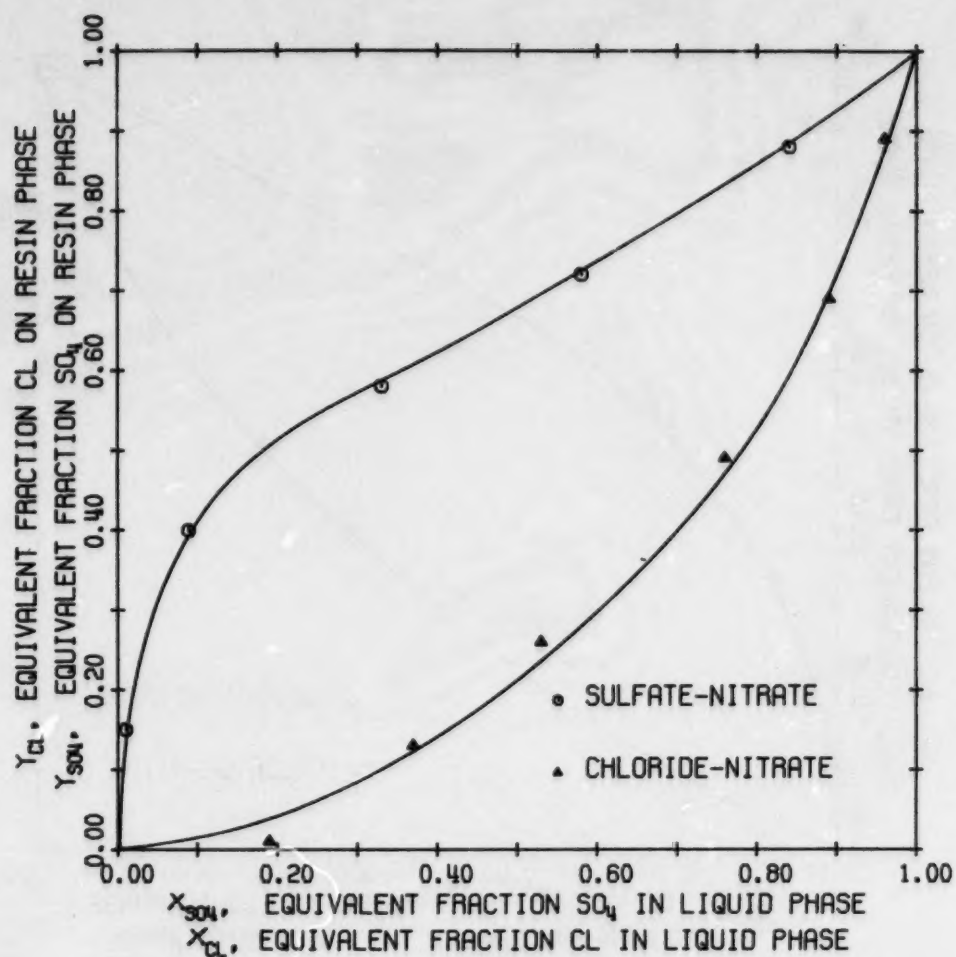
RESIN NUMBER 27
 IONAC ASB-1, MICROPOROUS GEL
 STYRENE-DVB MATRIX
 TYPE I, QUATERNARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.4 MEQ/ML

FIGURE A27
 25° C, BINARY ION-EXCHANGE ISOTHERM



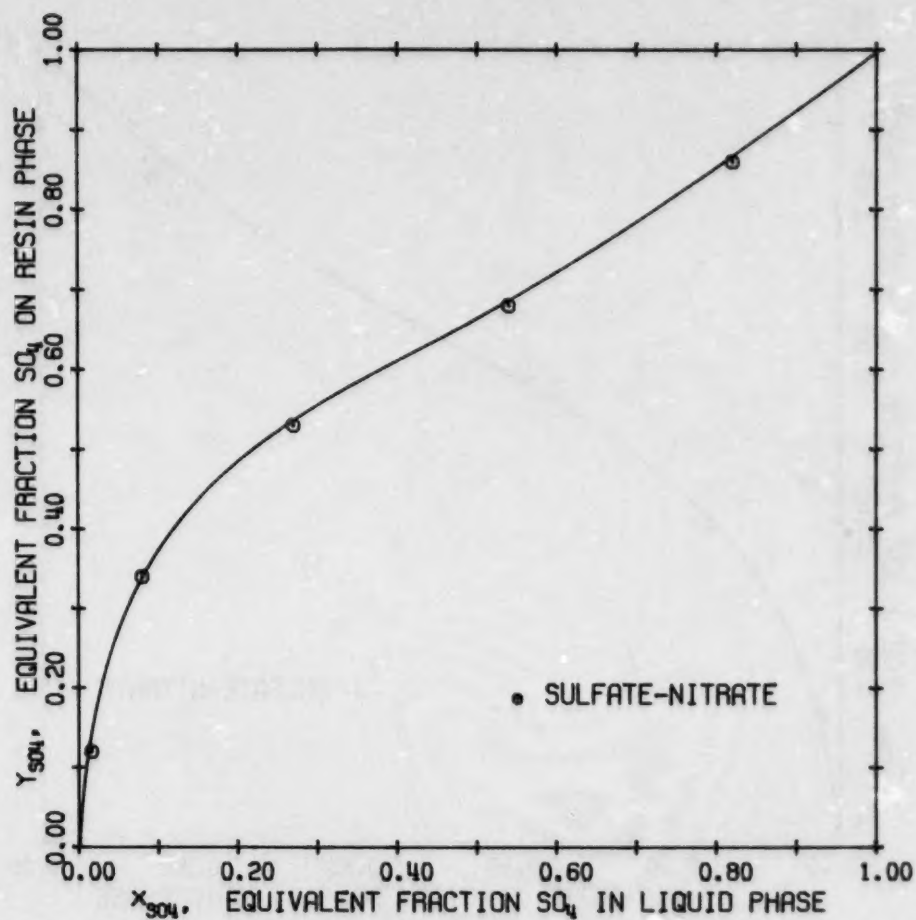
RESIN NUMBER 28
IONAC A-641, FIXED MACROPOROUS RESIN
STYRENE-DVB MATRIX
TYPE I, QUATERNARY-AMINE FUNCTIONALITY
TOTAL CAPACITY=1.16 MEQ/ML

FIGURE A28
25° C, BINARY ION-EXCHANGE ISOTHERM



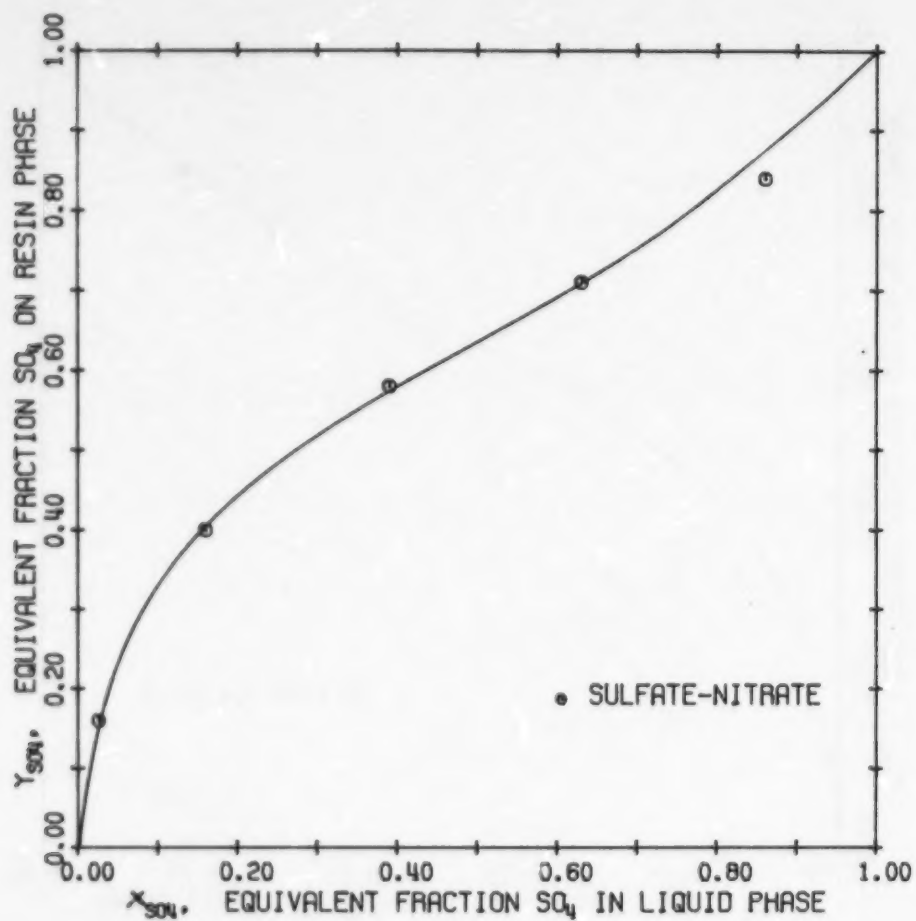
RESIN NUMBER 29
IONAC ASB-2, MICROPOROUS GEL
STYRENE-DVB MATRIX
TYPE II, QUATERNARY-AMINE FUNCTIONALITY
TOTAL CAPACITY=1.52 MEQ/ML

FIGURE A29
25° C, BINARY ION-EXCHANGE ISOTHERM



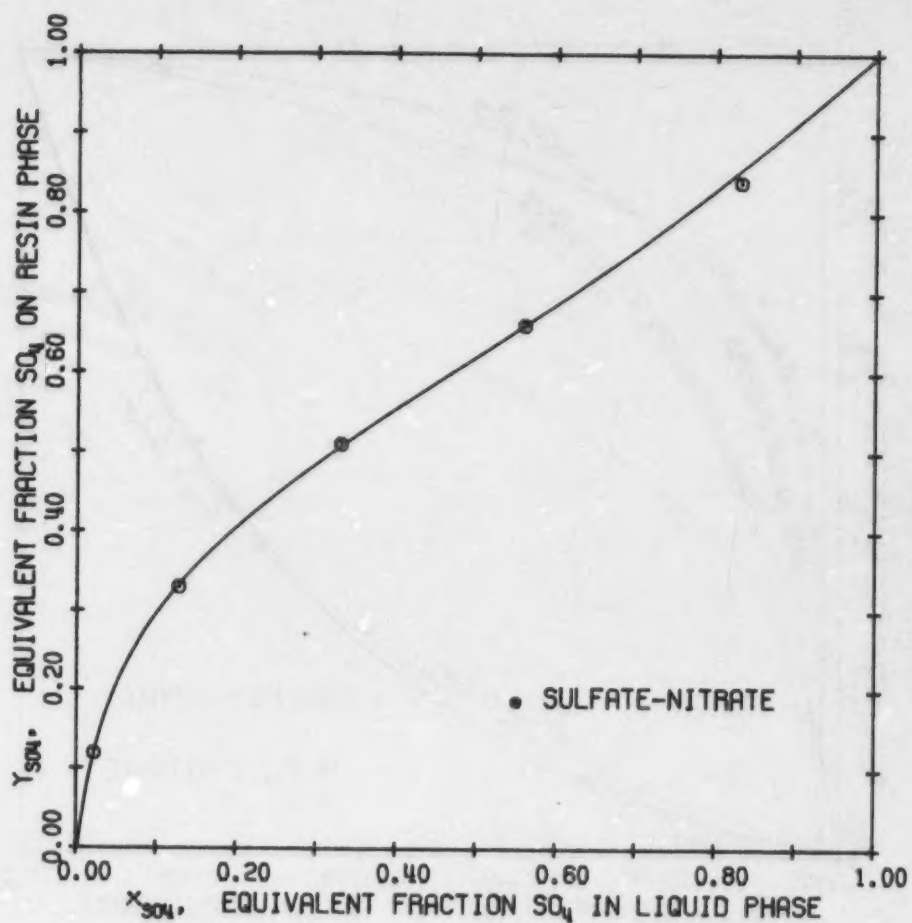
RESIN NUMBER 30
 IONAC ASB-1P, "IMPROVED" POROSITY GEL
 STYRENE-DVB MATRIX
 TYPE I, QUATERNARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.35 MEQ/ML

FIGURE A30
 25° C, BINARY ION-EXCHANGE ISOTHERM



RESIN NUMBER 31
 IONAC A-540, "IMPROVED" POROSITY GEL
 POLYSTYRENE MATRIX
 TYPE I, QUATERNARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.0 MEQ/ML

FIGURE A31
 25° C, BINARY ION-EXCHANGE ISOTHERM



RESIN NUMBER 32
 IONAC AFP-100, MACROPOROUS RESIN
 STYRENE-DVB MATRIX
 TYPE I, QUATERNARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY=1.2 MEQ/ML

FIGURE A32
 25° C, BINARY ION-EXCHANGE ISOTHERM

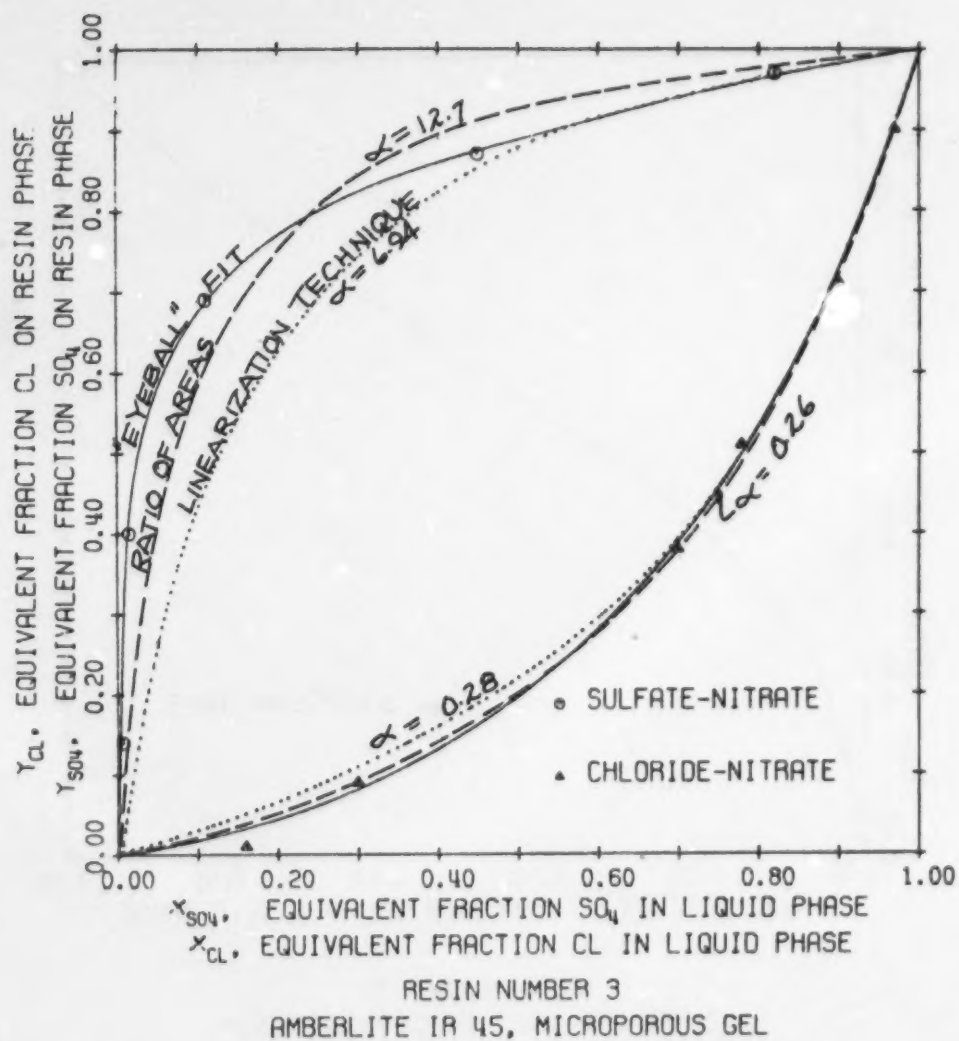


FIGURE NO. A33

COMPARISON OF CURVE FITTING TECHNIQUES
 ASSUMING
 CONSTANT SEPARATION FACTOR

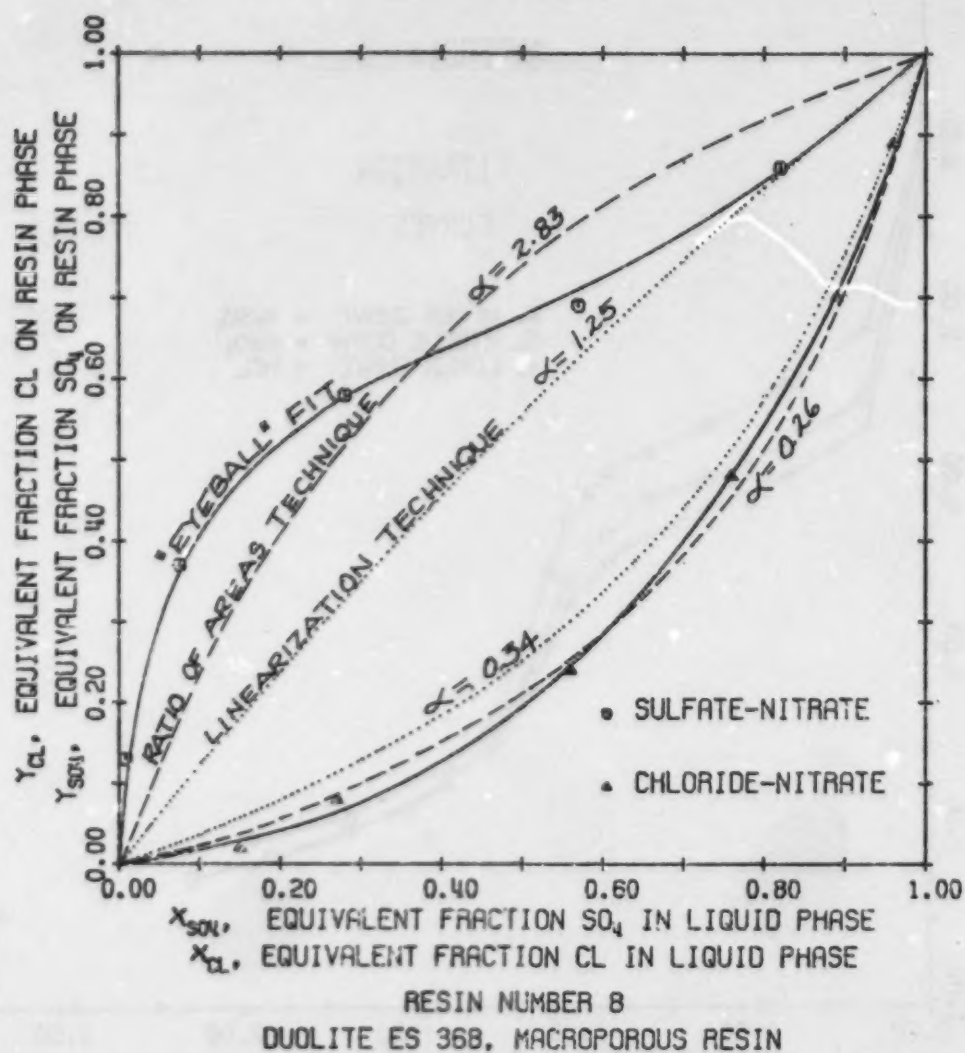
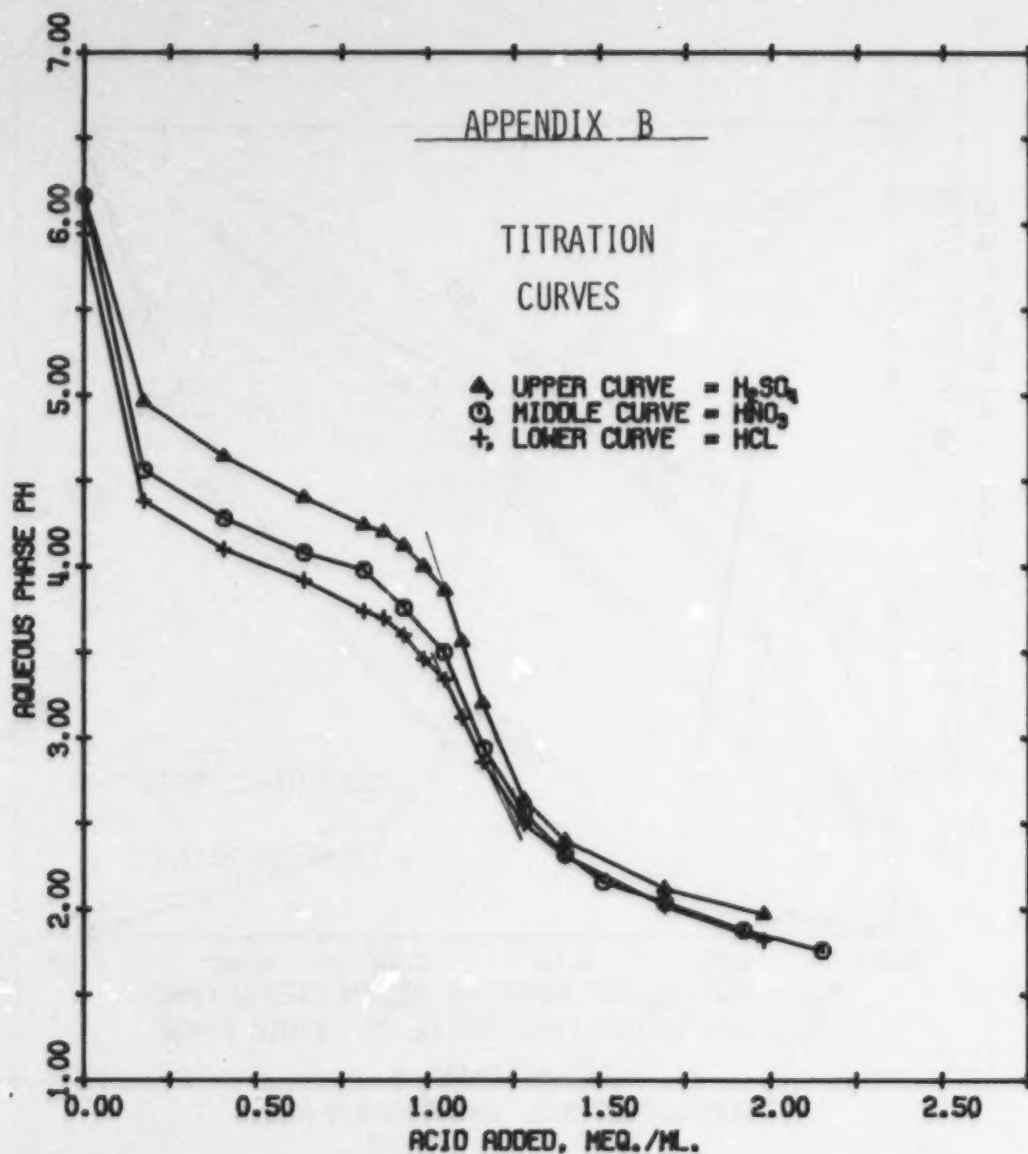
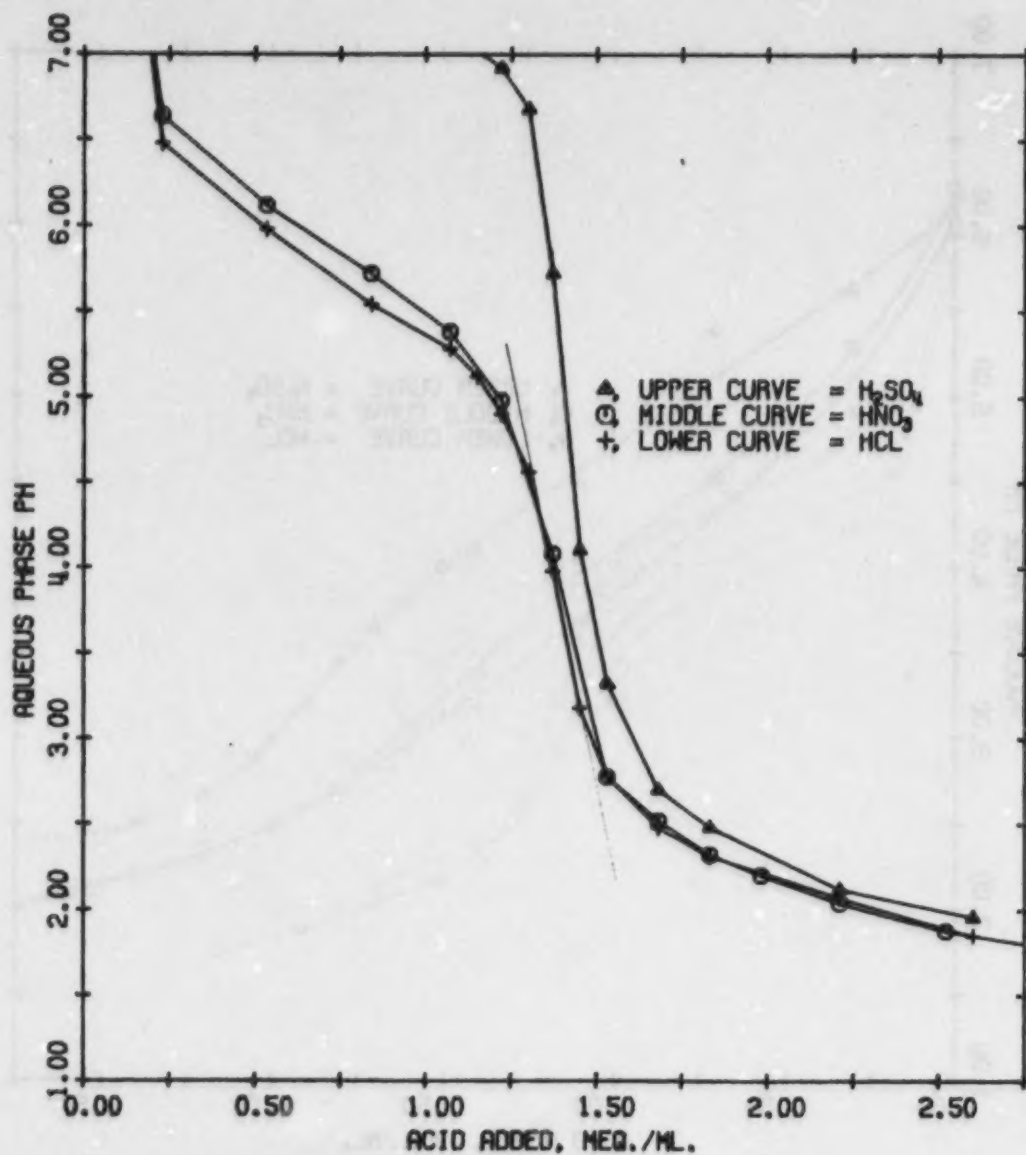


FIGURE NO. A34

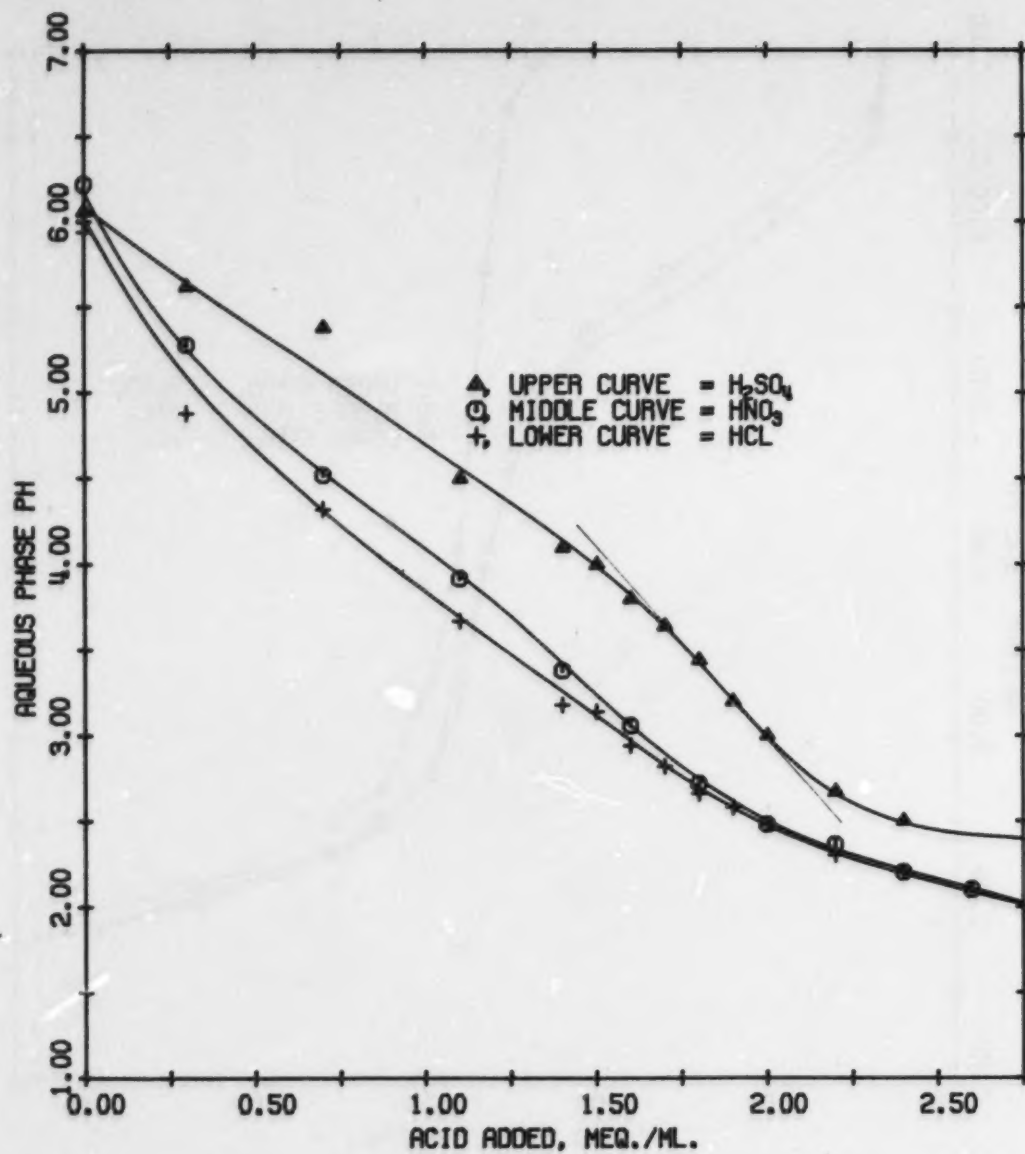
COMPARISON OF CURVE FITTING TECHNIQUES
ASSUMING
CONSTANT SEPARATION FACTOR



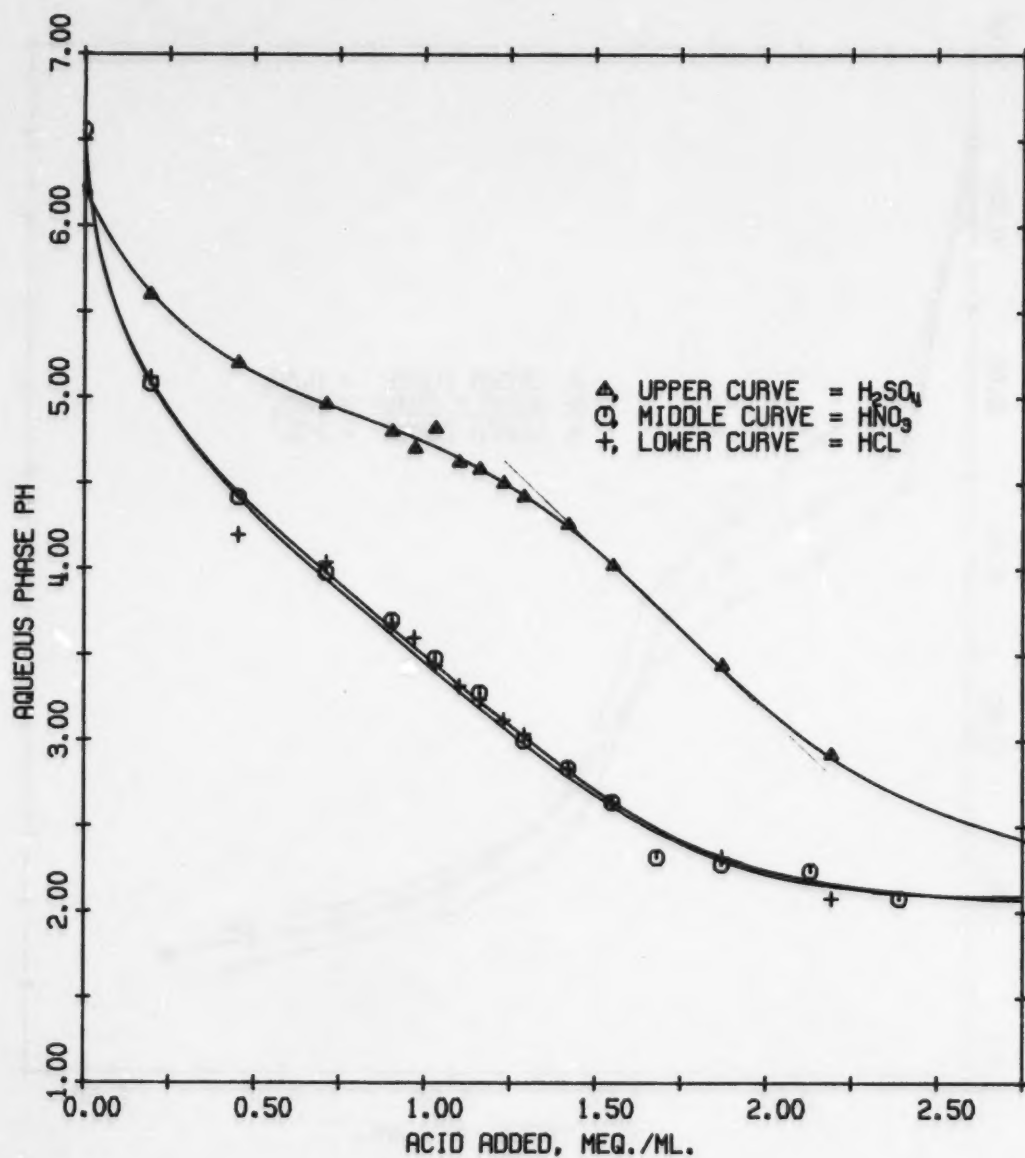
AMBERLITE IRA 93, MACROPOROUS RESIN
STYRENE-DVB MATRIX
TERTIARY-AMINE FUNCTIONALITY
TOTAL CAPACITY = 1.25 MEQ./ML.
FIGURE B1
RESIN NO. 1 TITRATION CURVES



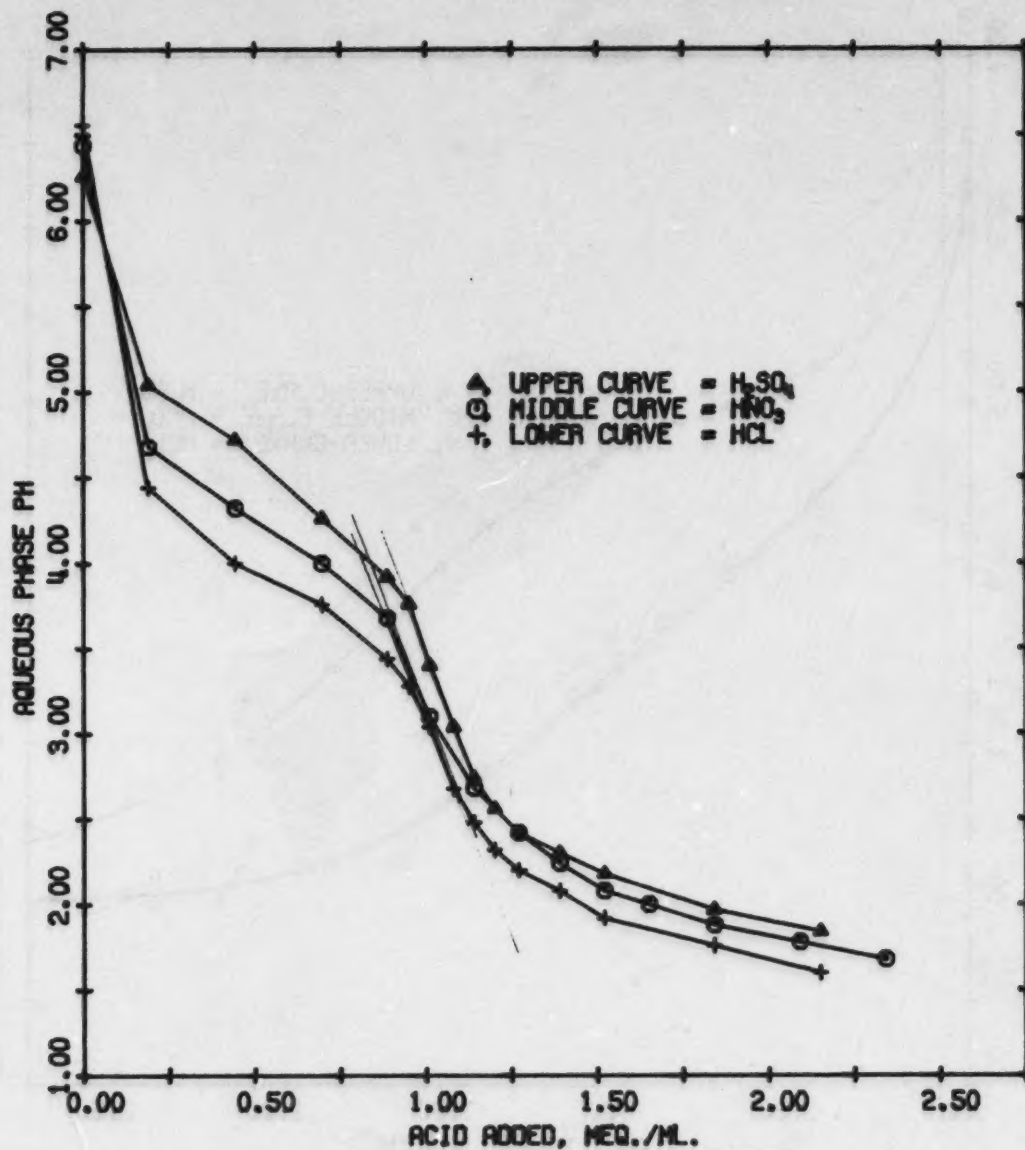
AMBERLITE IRA 68, MICROPOROUS GEL
POLYACRYLIC MATRIX
TERTIARY-AMINE FUNCTIONALITY
TOTAL CAPACITY = 1.6 MEQ./ML.
FIGURE B2
RESIN NO. 2 TITRATION CURVES



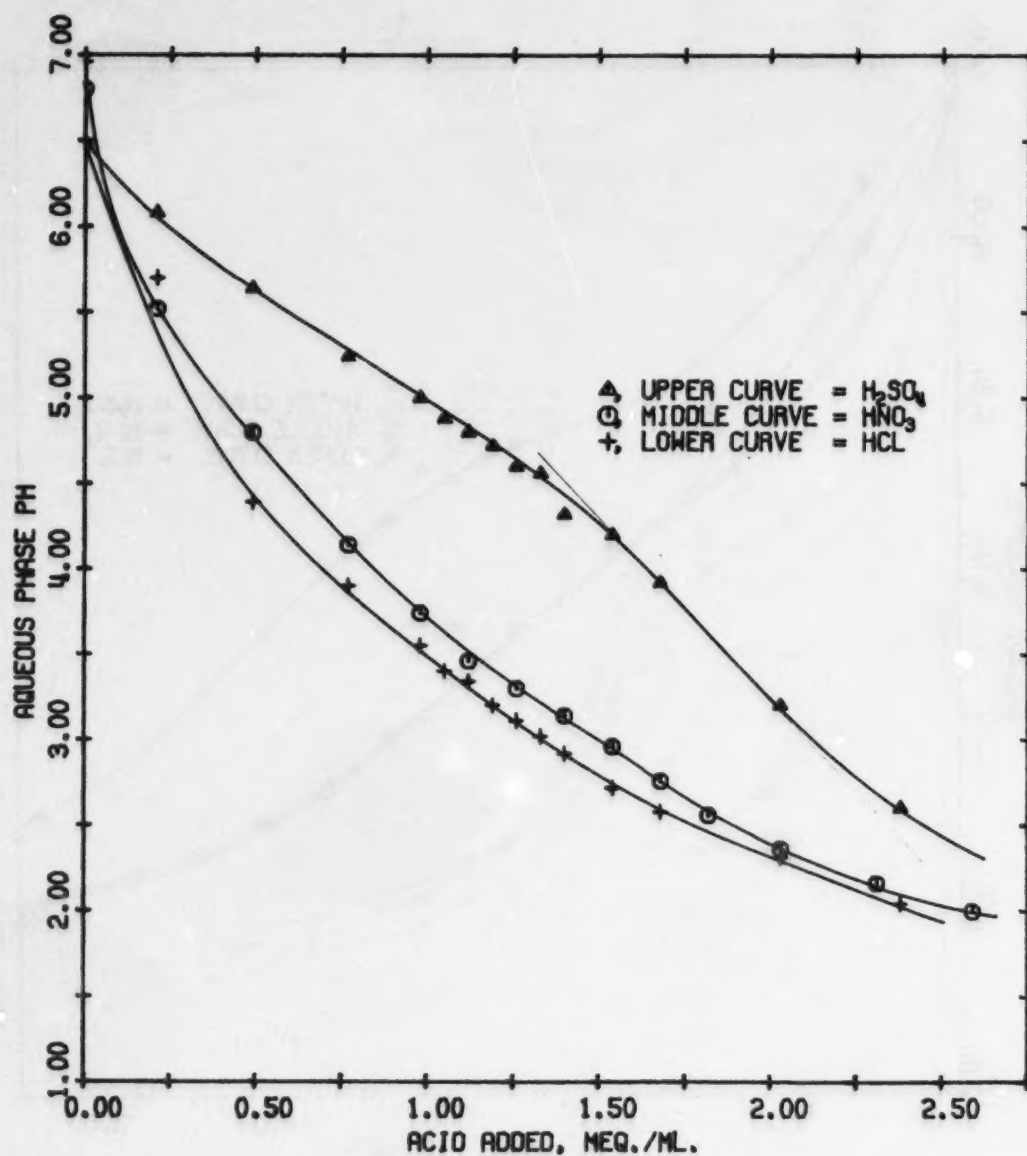
AMBERLITE IR 45, MICROPOROUS GEL
STYRENE-DVB MATRIX
POLYAMINE FUNCTIONALITY
TOTAL CAPACITY = 1.9 MEQ./ML.
FIGURE B3
RESIN NO. 3 TITRATION CURVES



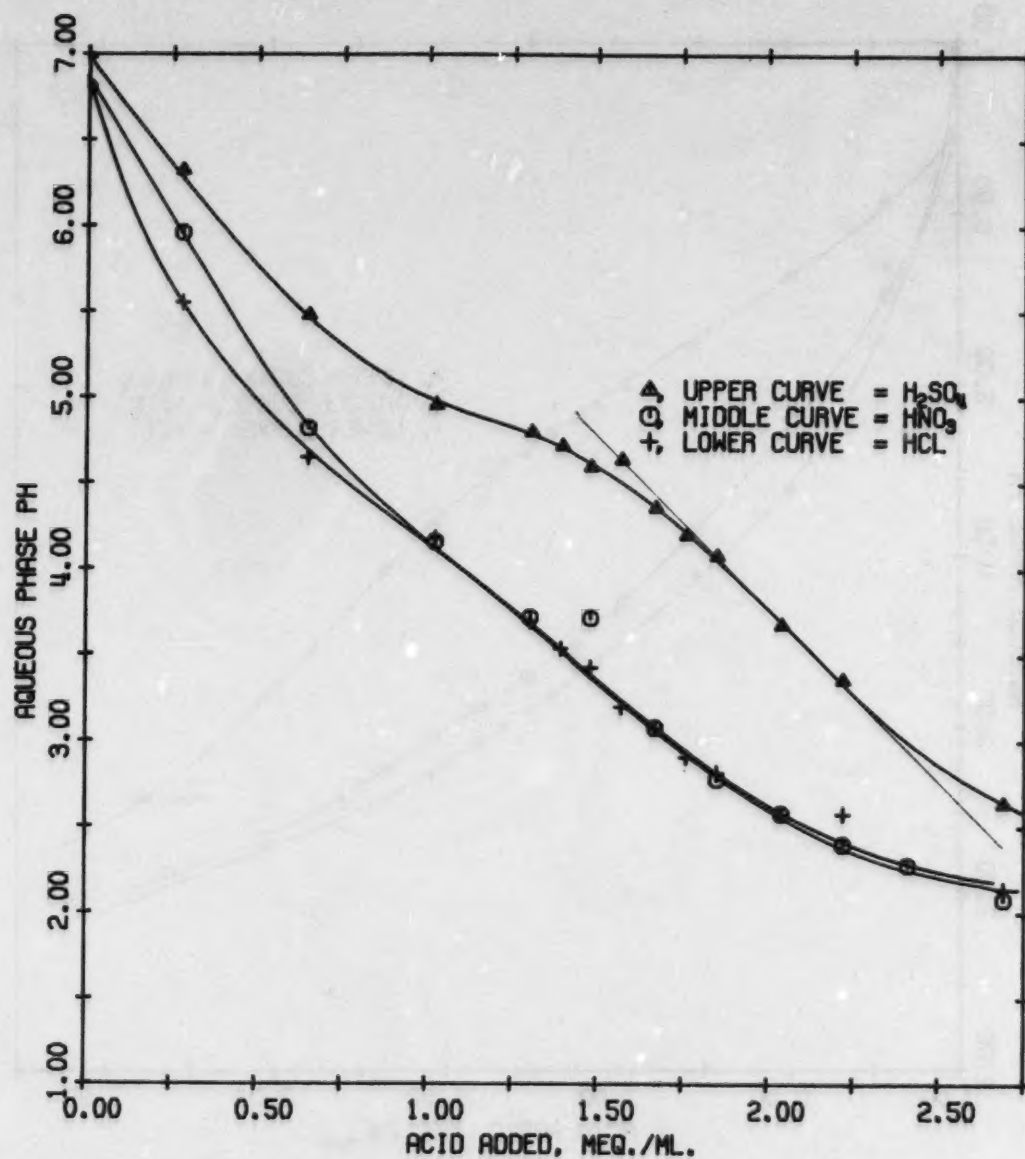
DOWEX WGR, MICROPOROUS GEL
EPOXY-AMINE MATRIX
POLYAMINE FUNCTIONALITY
TOTAL CAPACITY = 1.0 MEQ./ML.
FIGURE B4
RESIN NO. 4 TITRATION CURVES



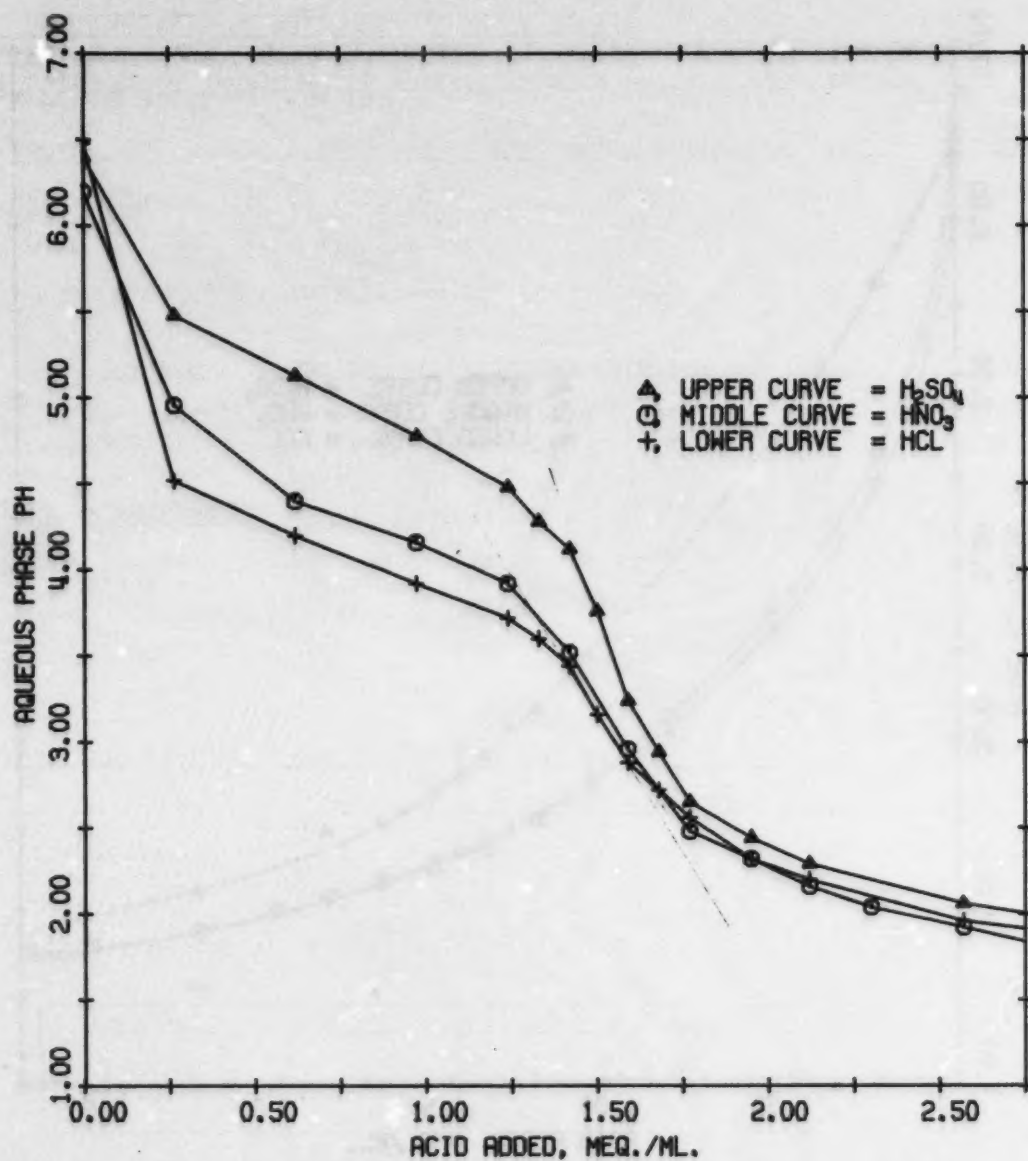
DOWEX MWA-1, MACROPOROUS RESIN
STYRENE-DVB MATRIX
TERTIARY-AMINE FUNCTIONALITY
TOTAL CAPACITY = 1.1 MEQ./ML.
FIGURE B5
RESIN NO. 5 TITRATION CURVES



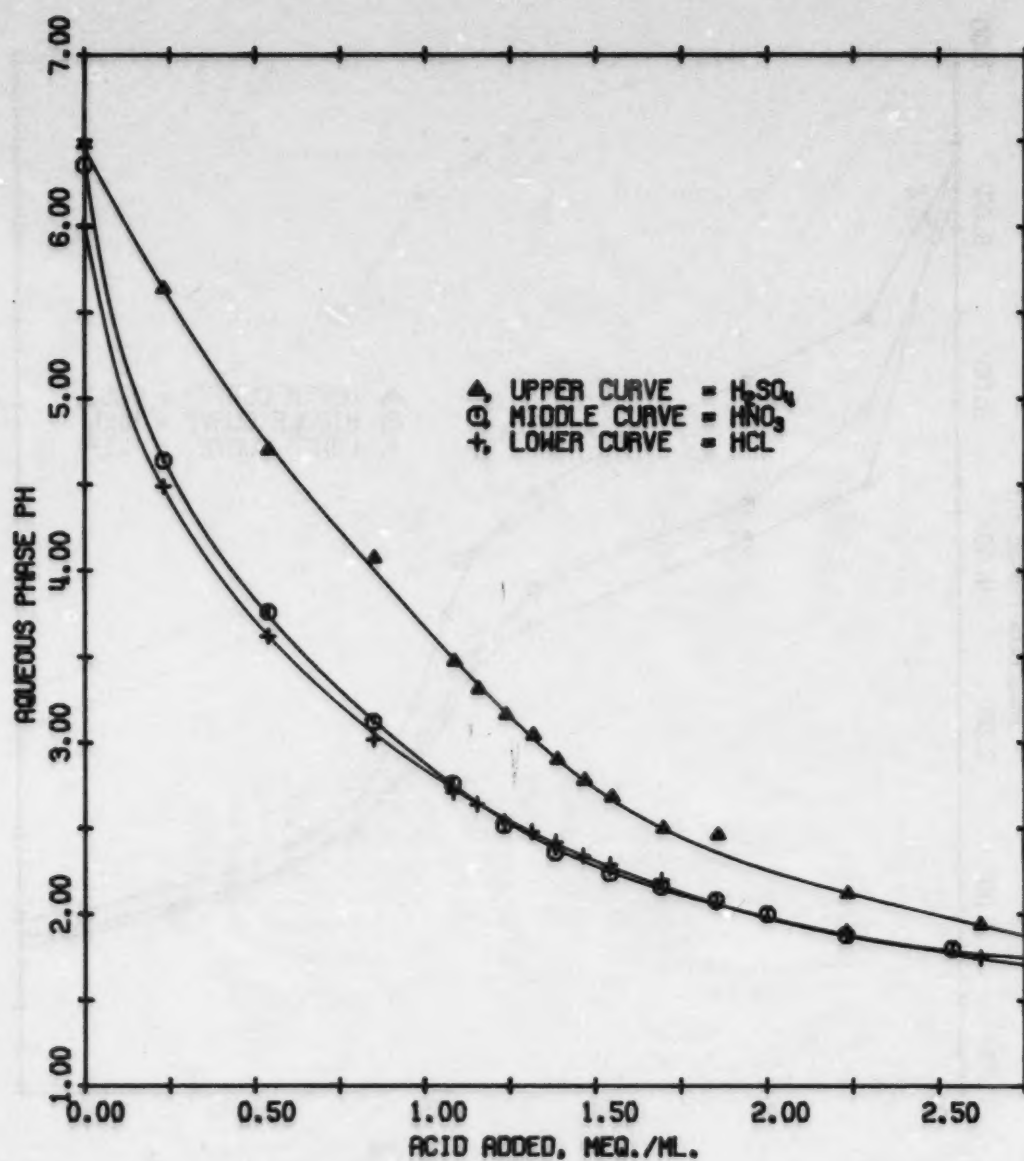
DUOLITE A-7, MACROPOROUS, GRANULAR RESIN
PHENOL-FORMALDEHYDE MATRIX
SECONDARY-AMINE FUNCTIONALITY
(POLYAMINE TITRATION CURVE)
TOTAL CAPACITY = 2.4 MEQ./ML.
FIGURE B6
RESIN NO. 6 TITRATION CURVES



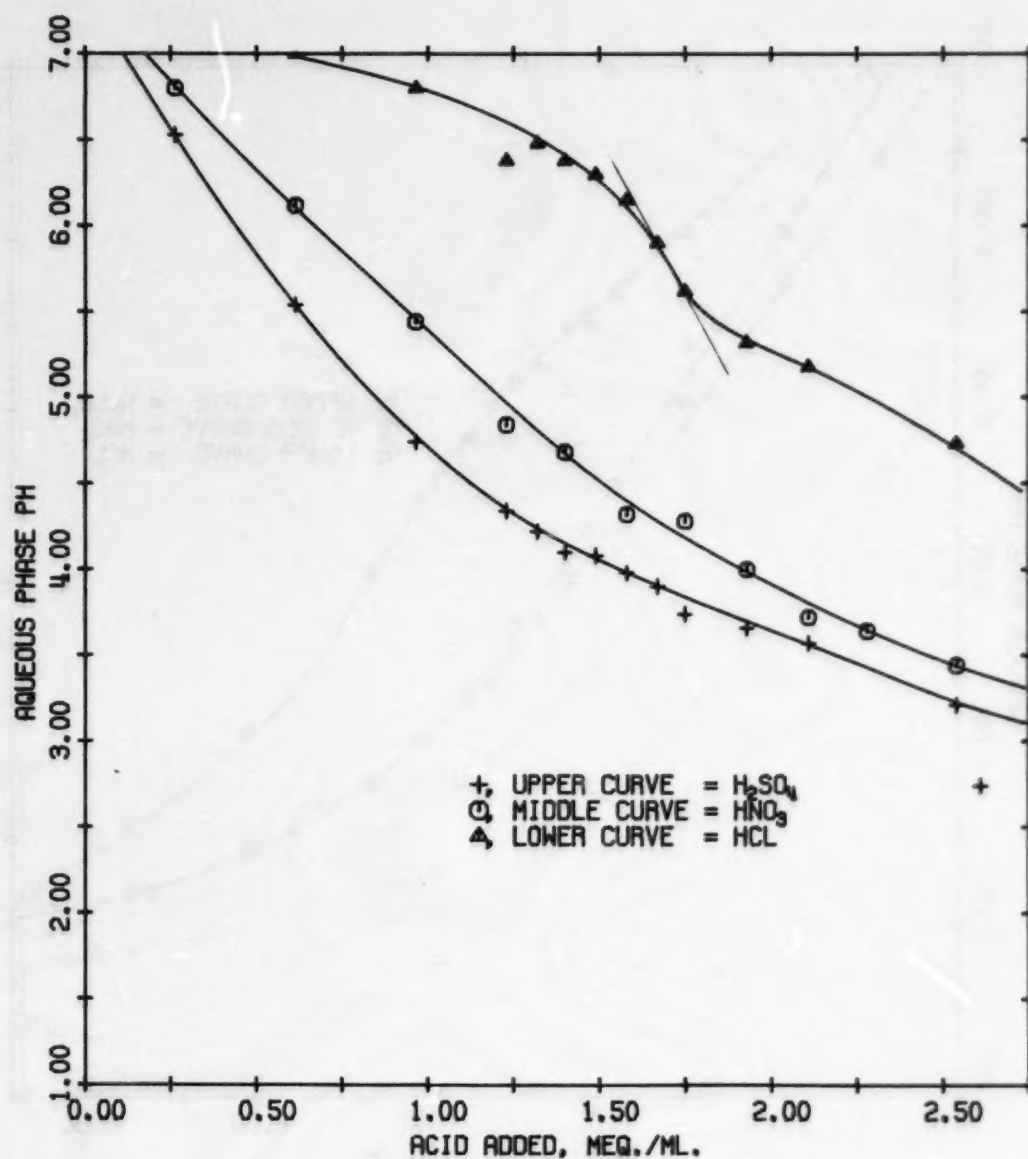
DUOLITE A 340, MICROPOROUS GEL
 EPOXY-AMINE MATRIX
 POLYAMINE FUNCTIONALITY
 TOTAL CAPACITY = 2.6 MEQ./ML.
 FIGURE B7
 RESIN NO. 7 TITRATION CURVES



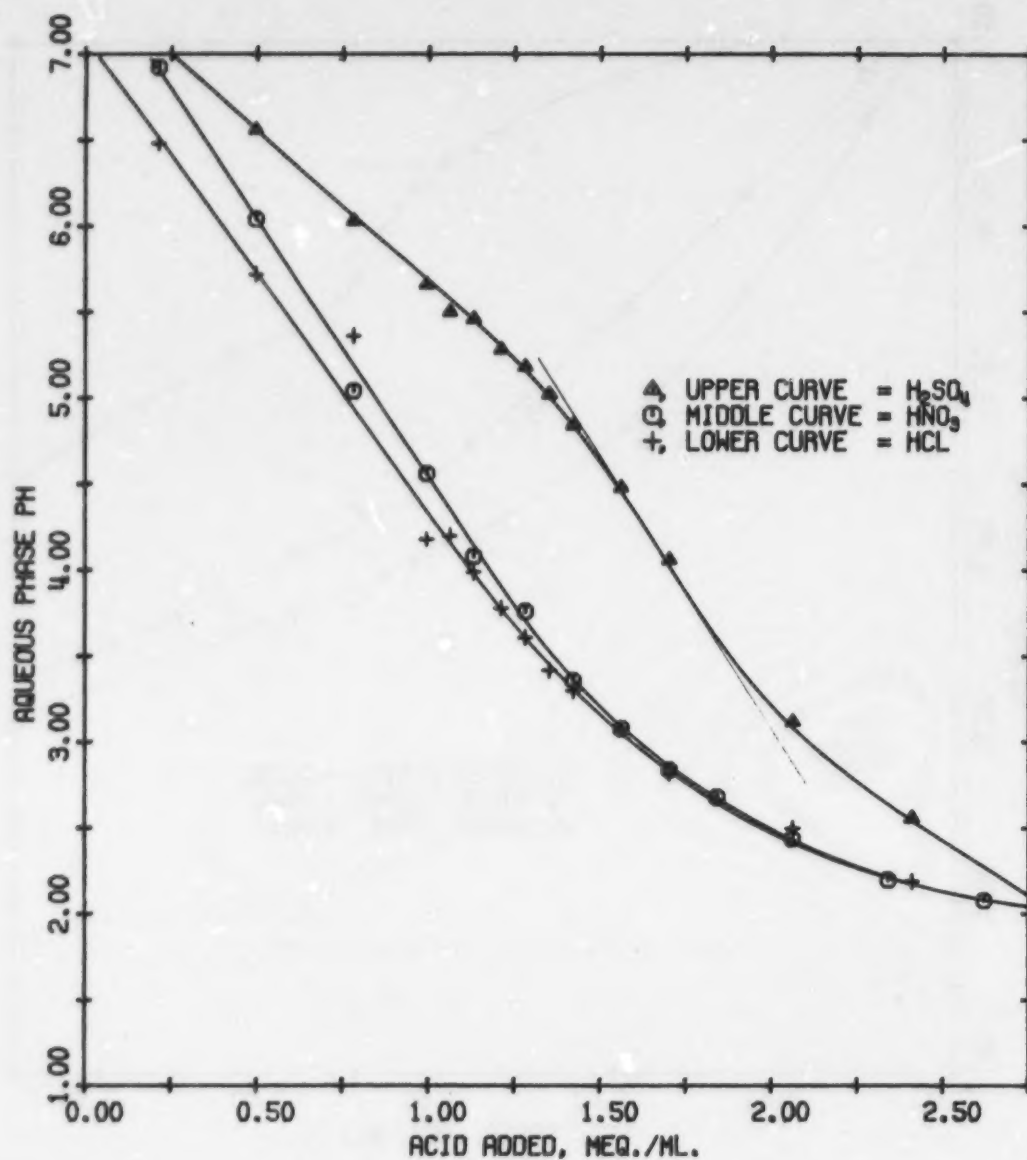
DUOLITE ES 368, MACROPOROUS RESIN
STYRENE-DVB MATRIX
TERTIARY-AMINE FUNCTIONALITY
TOTAL CAPACITY = 1.3 MEQ./ML.
FIGURE B8
RESIN NO. 8 TITRATION CURVES



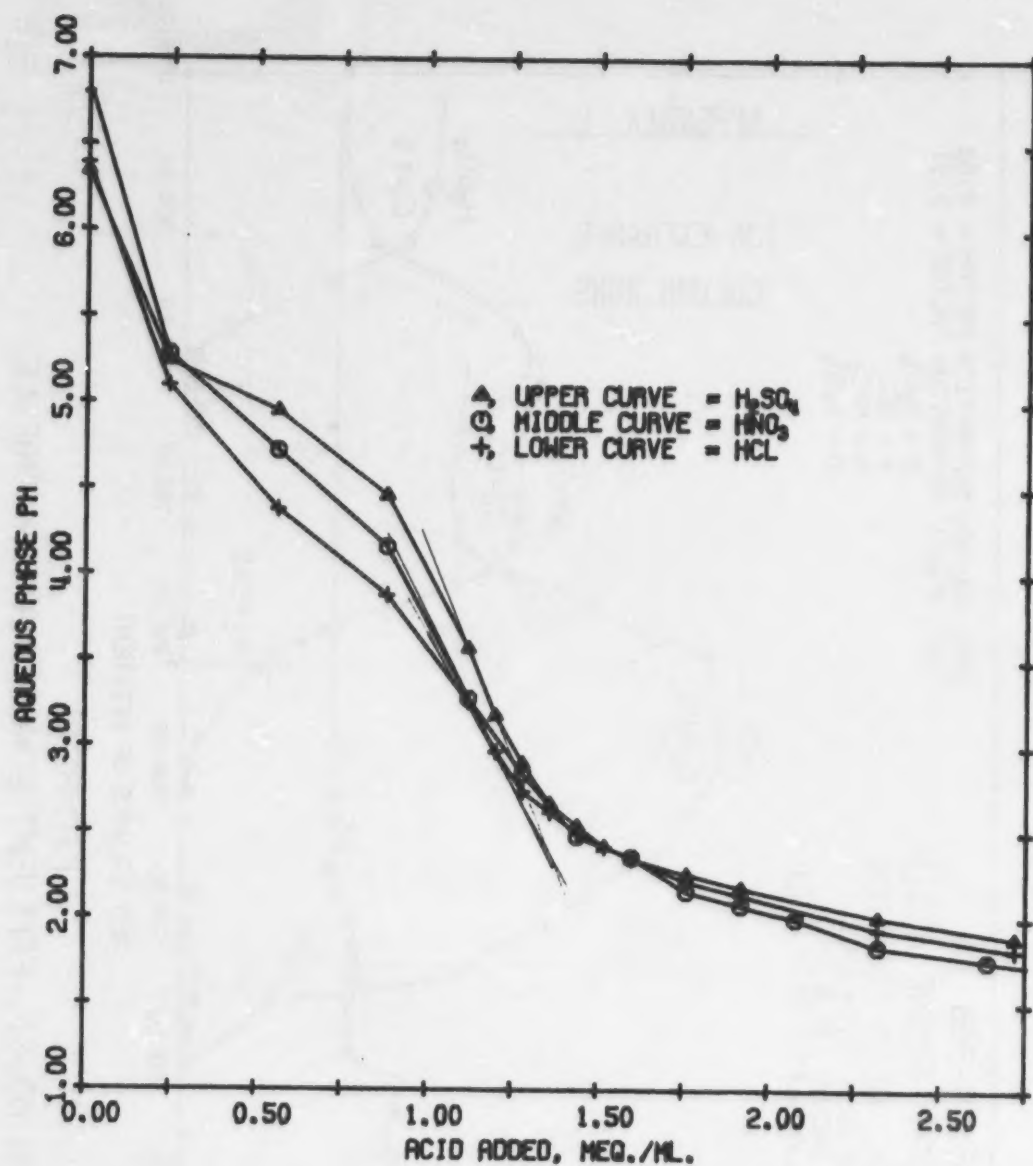
DUOLITE ES 561, MACROPOROUS GRANULAR RESIN
PHENOL-FORMALDEHYDE MATRIX
POLYAMINE FUNCTIONALITY
TOTAL CAPACITY = 2.0 MEQ./ML.
FIGURE B9
RESIN NO. 9 TITRATION CURVES



DUOLITE ES 374, MACROPOROUS RESIN
 POLYACRYLIC MATRIX
 TERTIARY-AMINE FUNCTIONALITY
 (POLYAMINE TITRATION CURVE)
 TOTAL CAPACITY = 3.0 MEQ./ML.
 FIGURE B10
 RESIN NO. 10 TITRATION CURVES



IONAC A-260, MICROPOROUS GRANULAR GEL
ALIPHATIC-AMINE MATRIX
POLYAMINE FUNCTIONALITY
TOTAL CAPACITY = 1.8 MEQ./ML.
FIGURE B11
RESIN NO. 11 TITRATION CURVES



IONAC AFP 329, MACROPOROUS RESIN
 STYRENE-DVB MATRIX
 TERTIARY-AMINE FUNCTIONALITY
 TOTAL CAPACITY = 1.25 MEQ./ML.
 FIGURE B12
 RESIN NO. 12 TITRATION CURVES

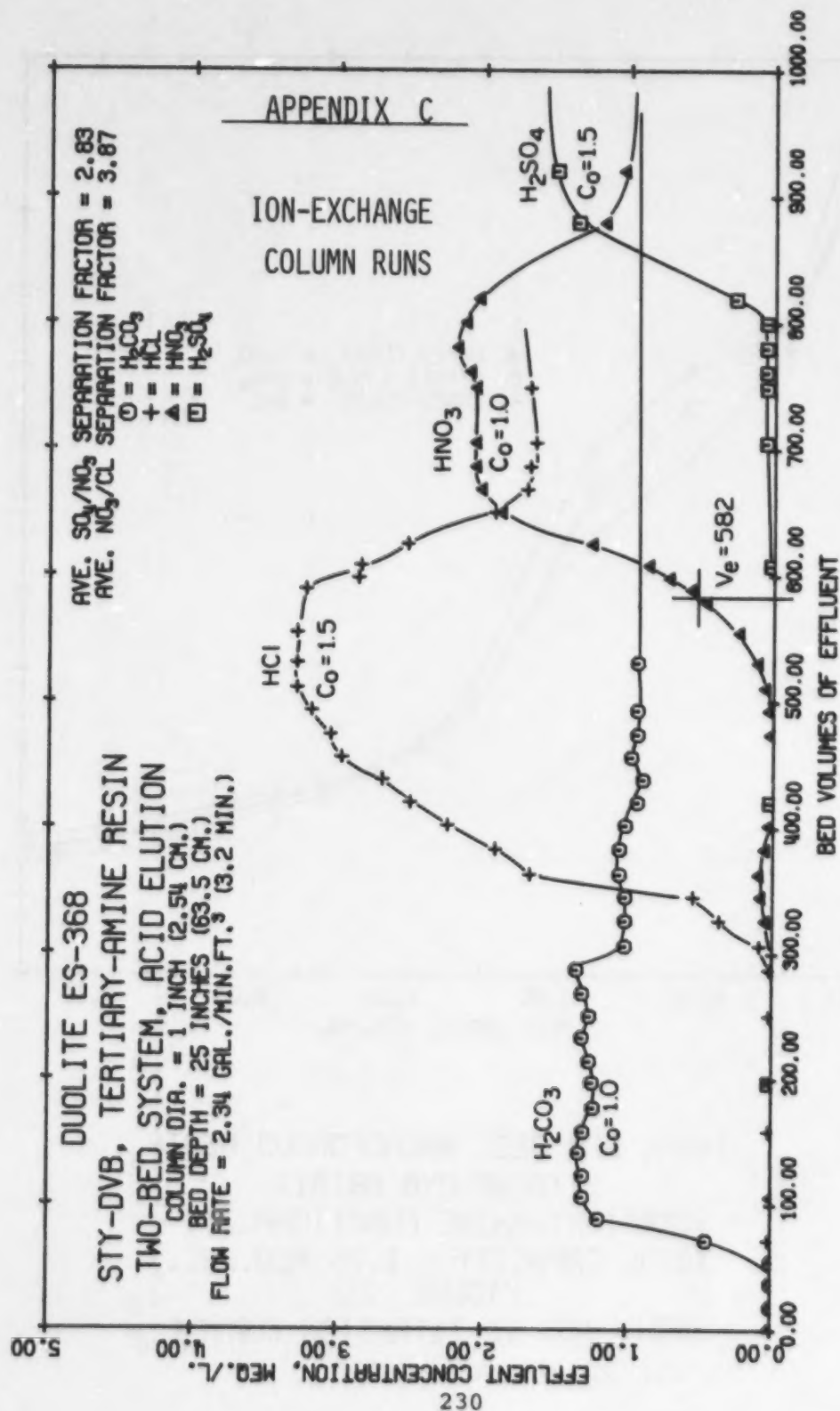


FIGURE C1
RUN NO. 1, EFFLUENT CONCENTRATION PROFILE

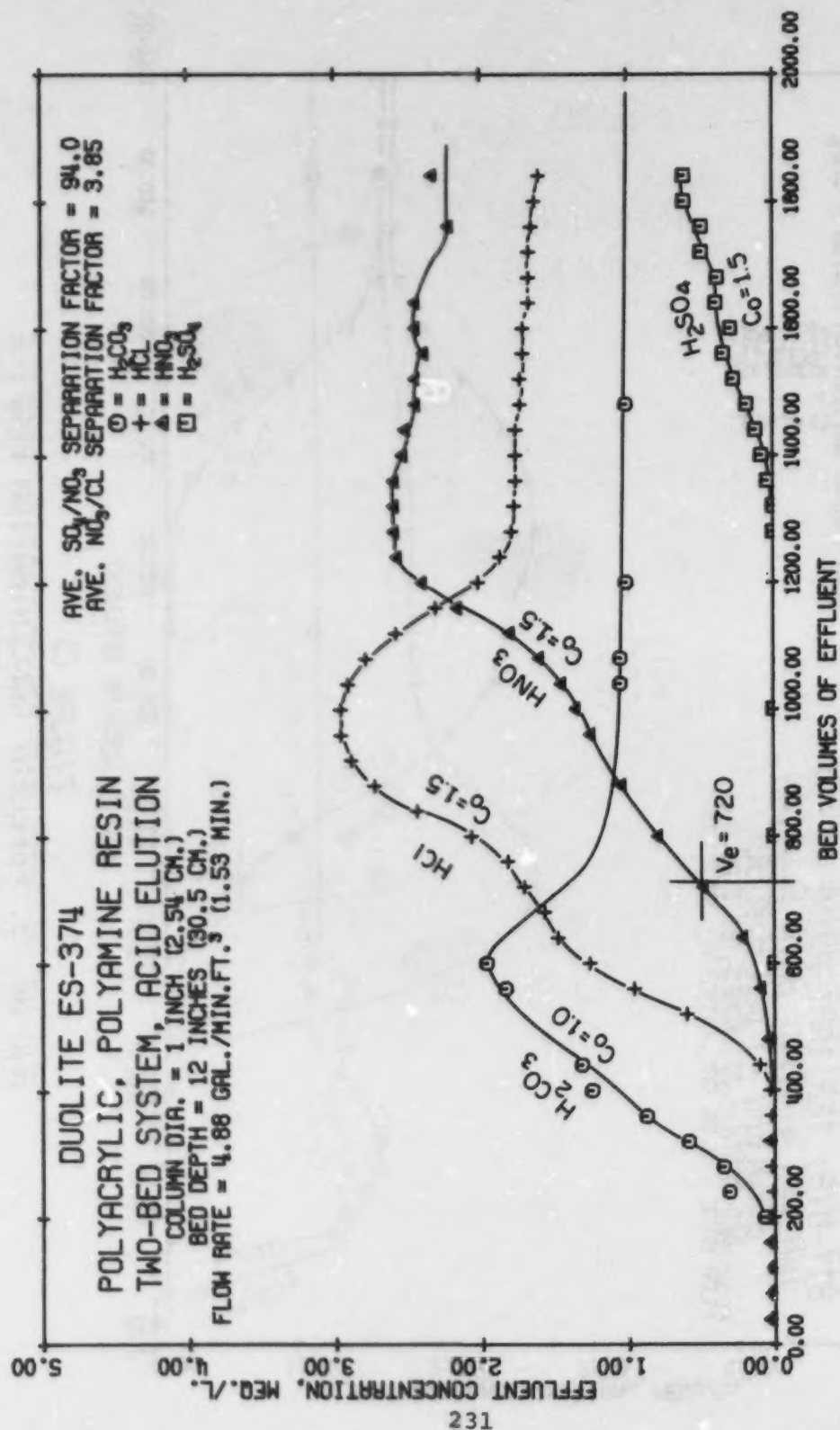


FIGURE C2
RUN NO. 2, EFFLUENT CONCENTRATION PROFILE

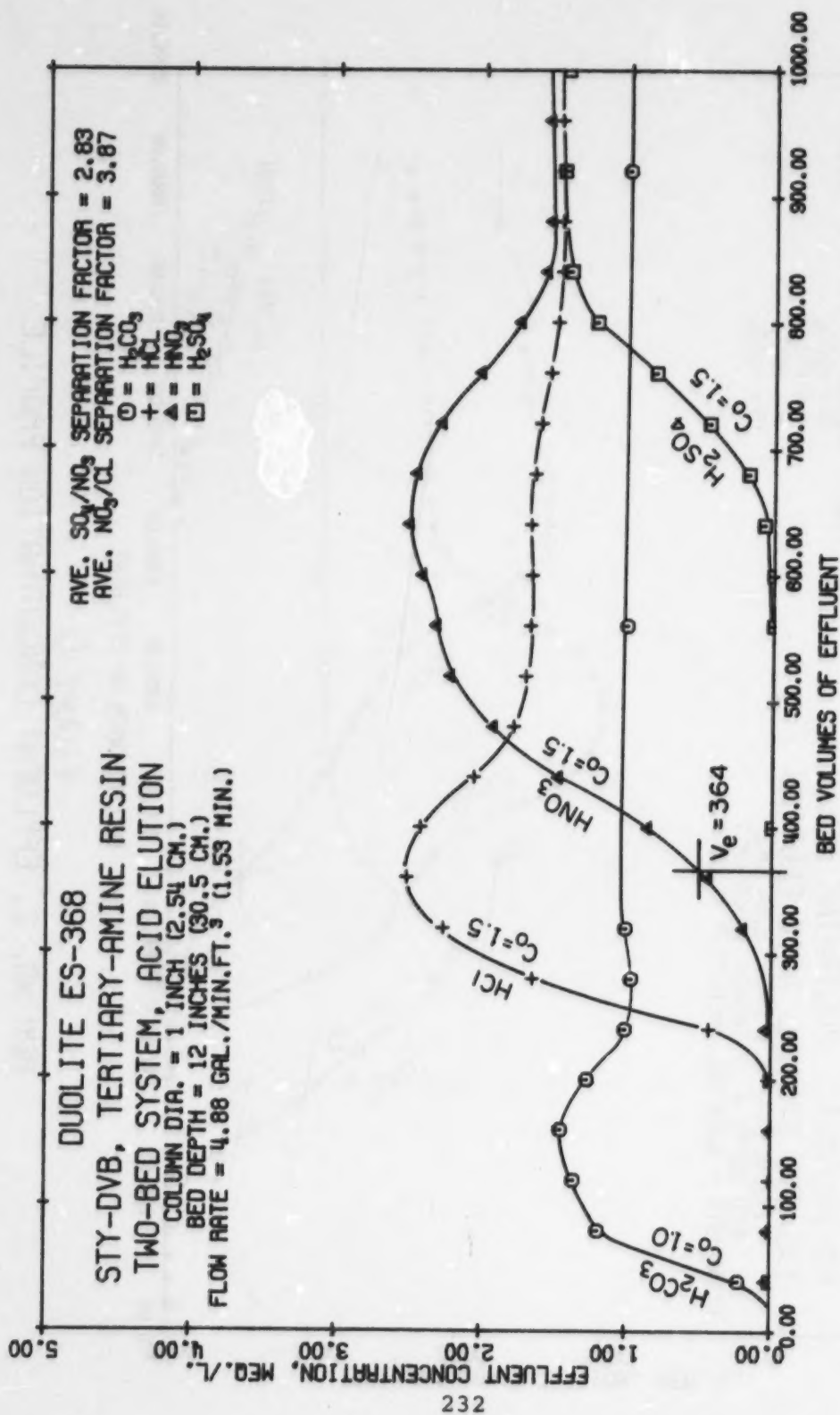


FIGURE C3
 RUN NO. 3, EFFLUENT CONCENTRATION PROFILE

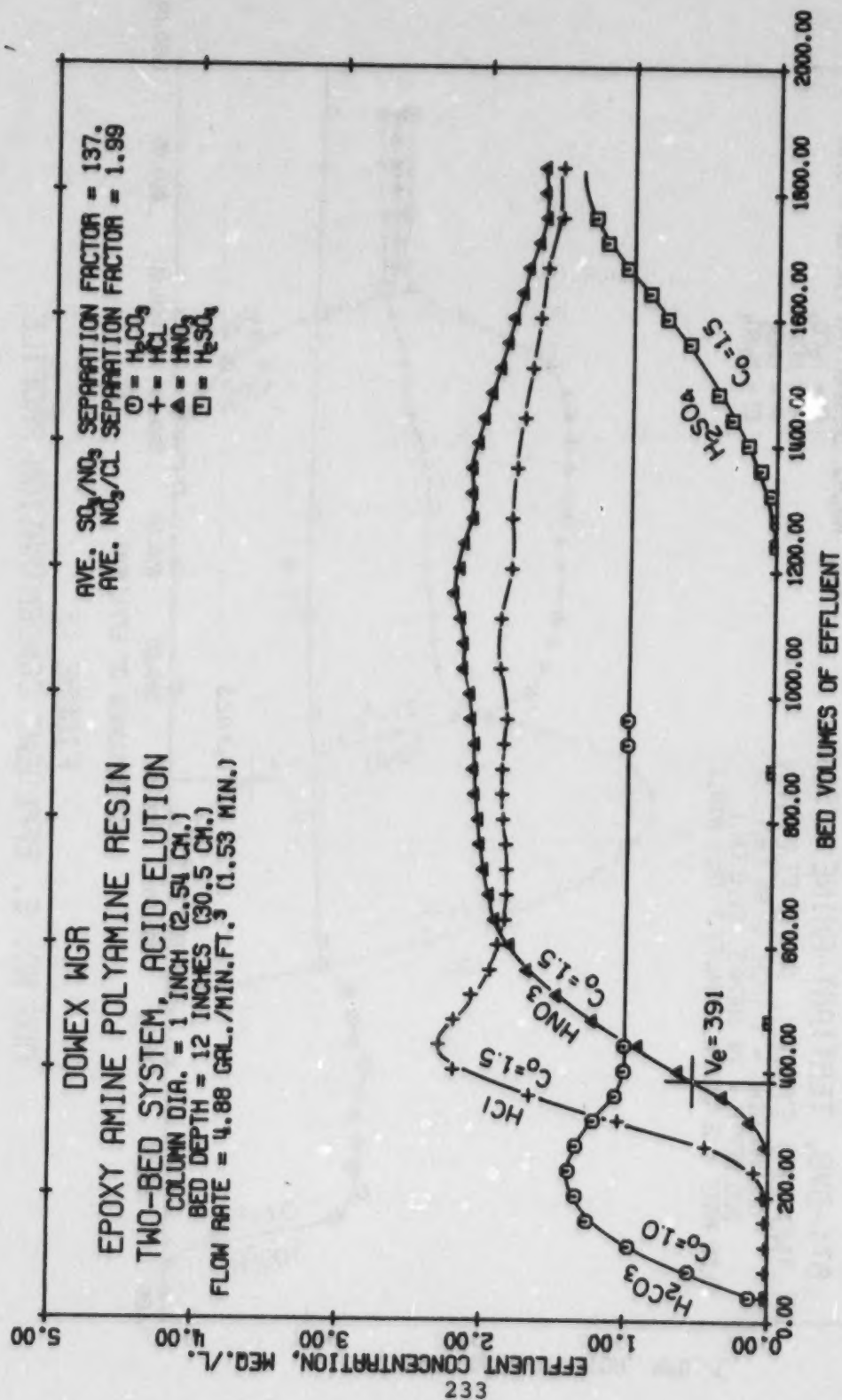


FIGURE C4

RUN NO. 4, EFFLUENT CONCENTRATION PROFILE

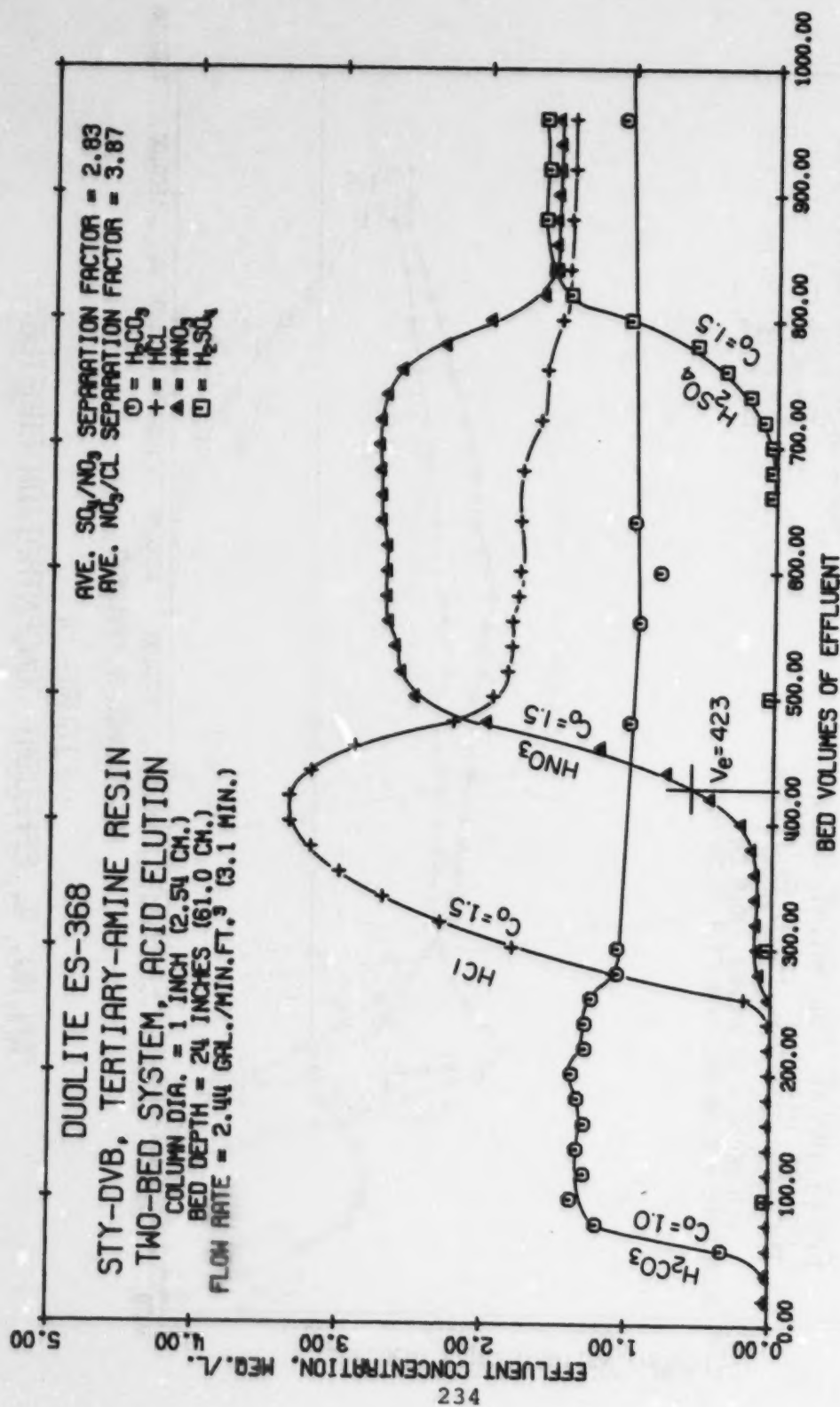


FIGURE C5
 RUN NO. 5, EFFLUENT CONCENTRATION PROFILE

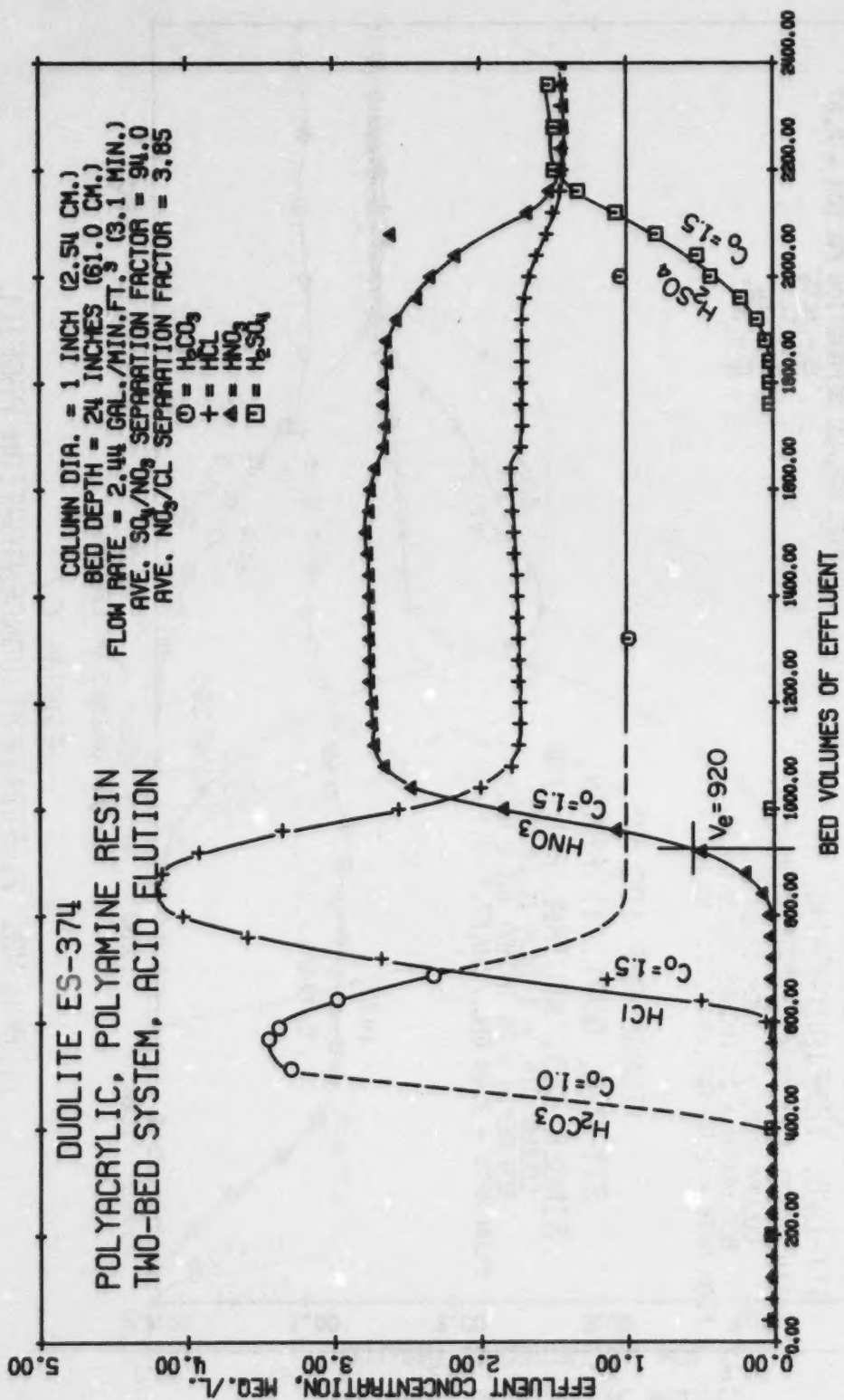


FIGURE C6
 RUN NO. 6, EFFLUENT CONCENTRATION PROFILE

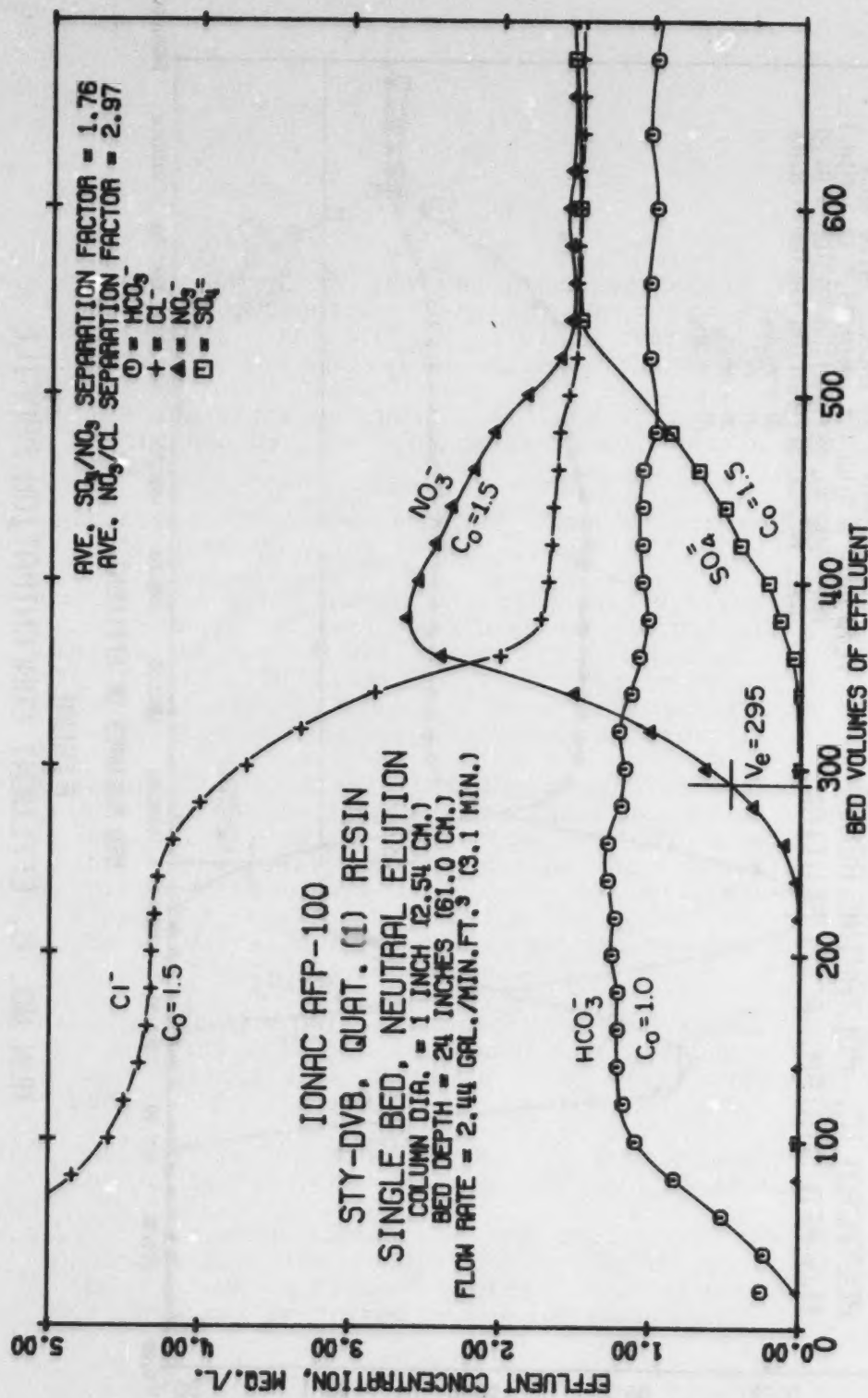


FIGURE C7
 RUN NO. 7, EFFLUENT CONCENTRATION PROFILE

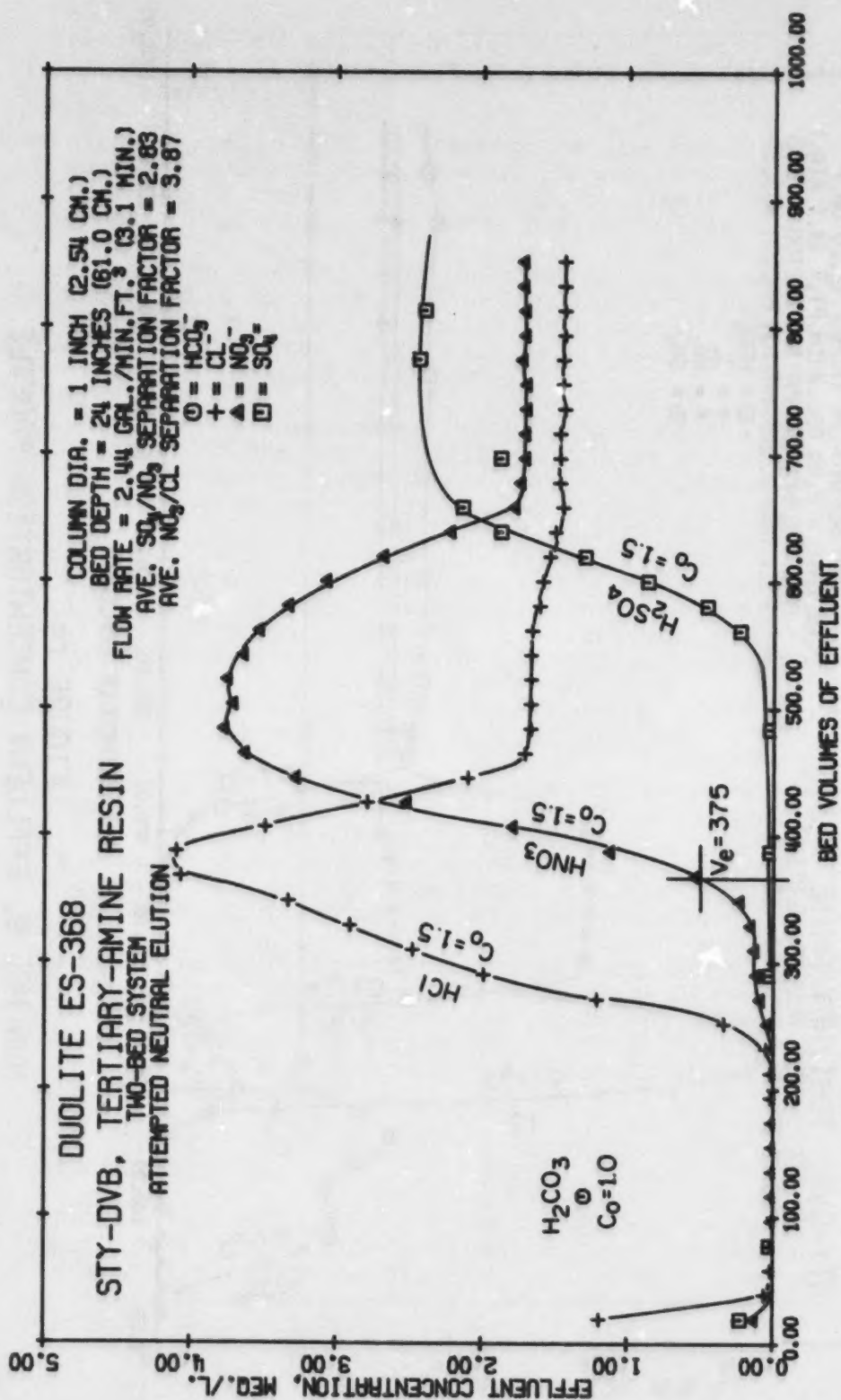


FIGURE C8
 RUN NO. 8, EFFLUENT CONCENTRATION PROFILE

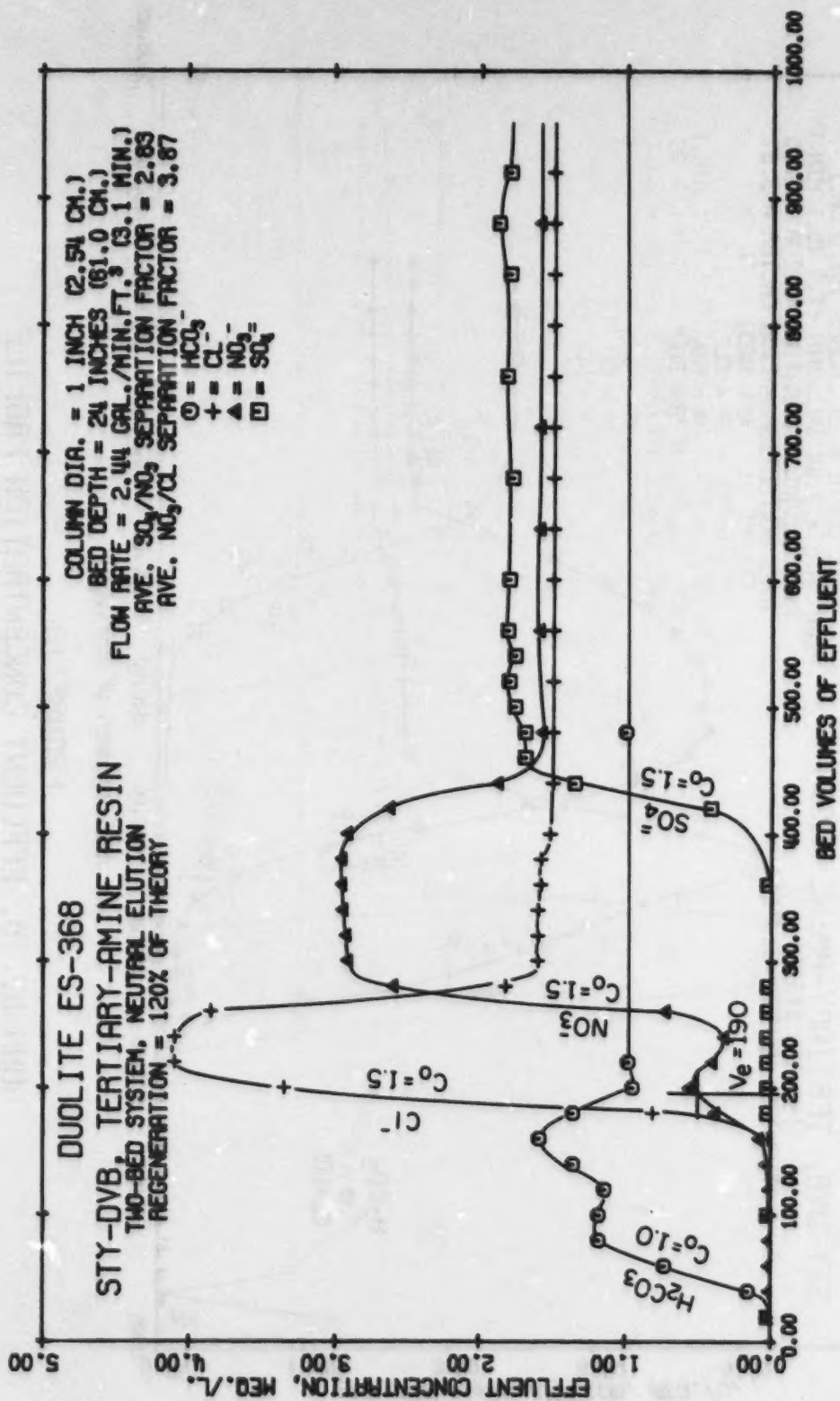


FIGURE C9
 RUN NO. 9. EFFLUENT CONCENTRATION PROFILE

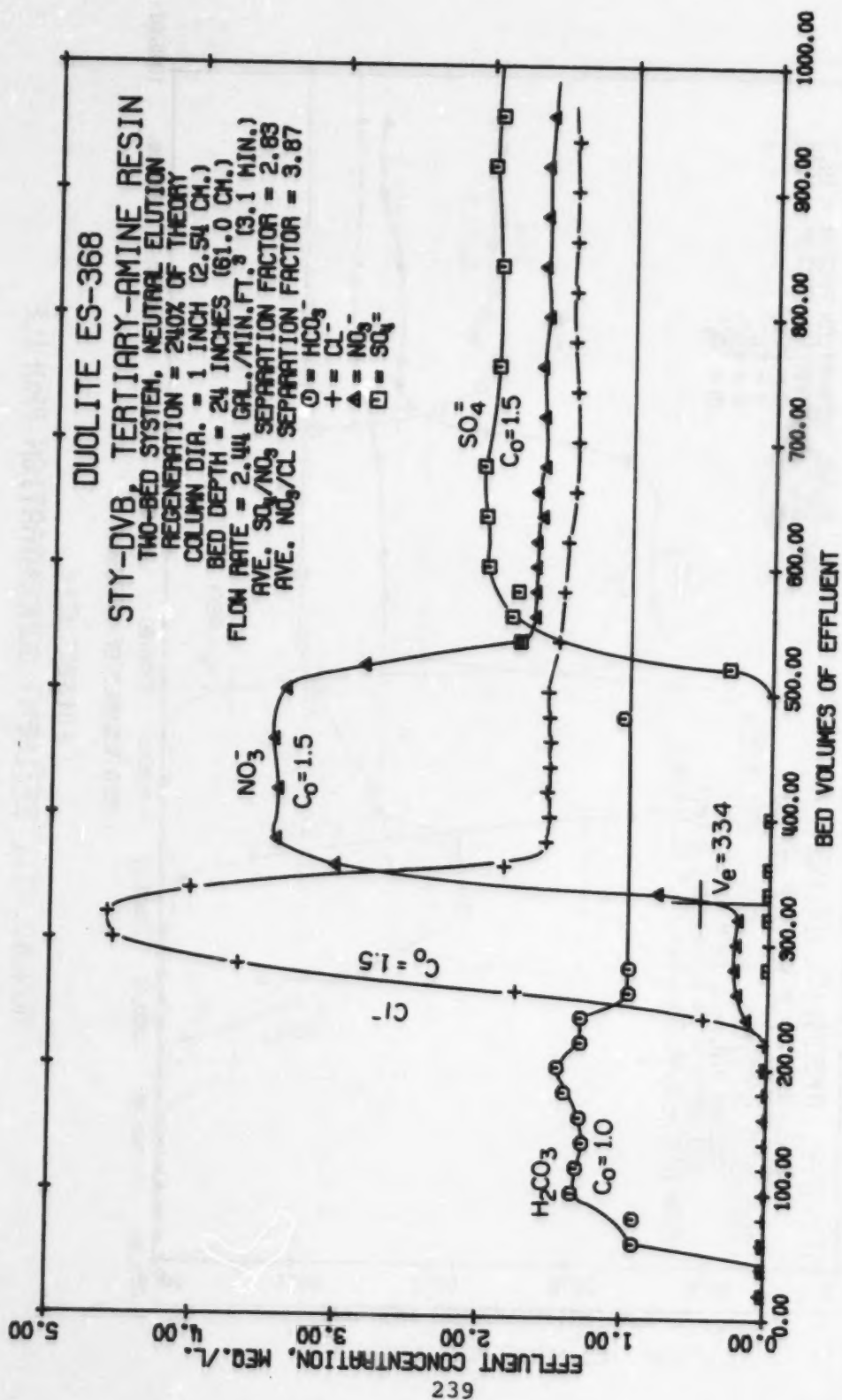


FIGURE C10

RUN NO. 10, EFFLUENT CONCENTRATION PROFILE

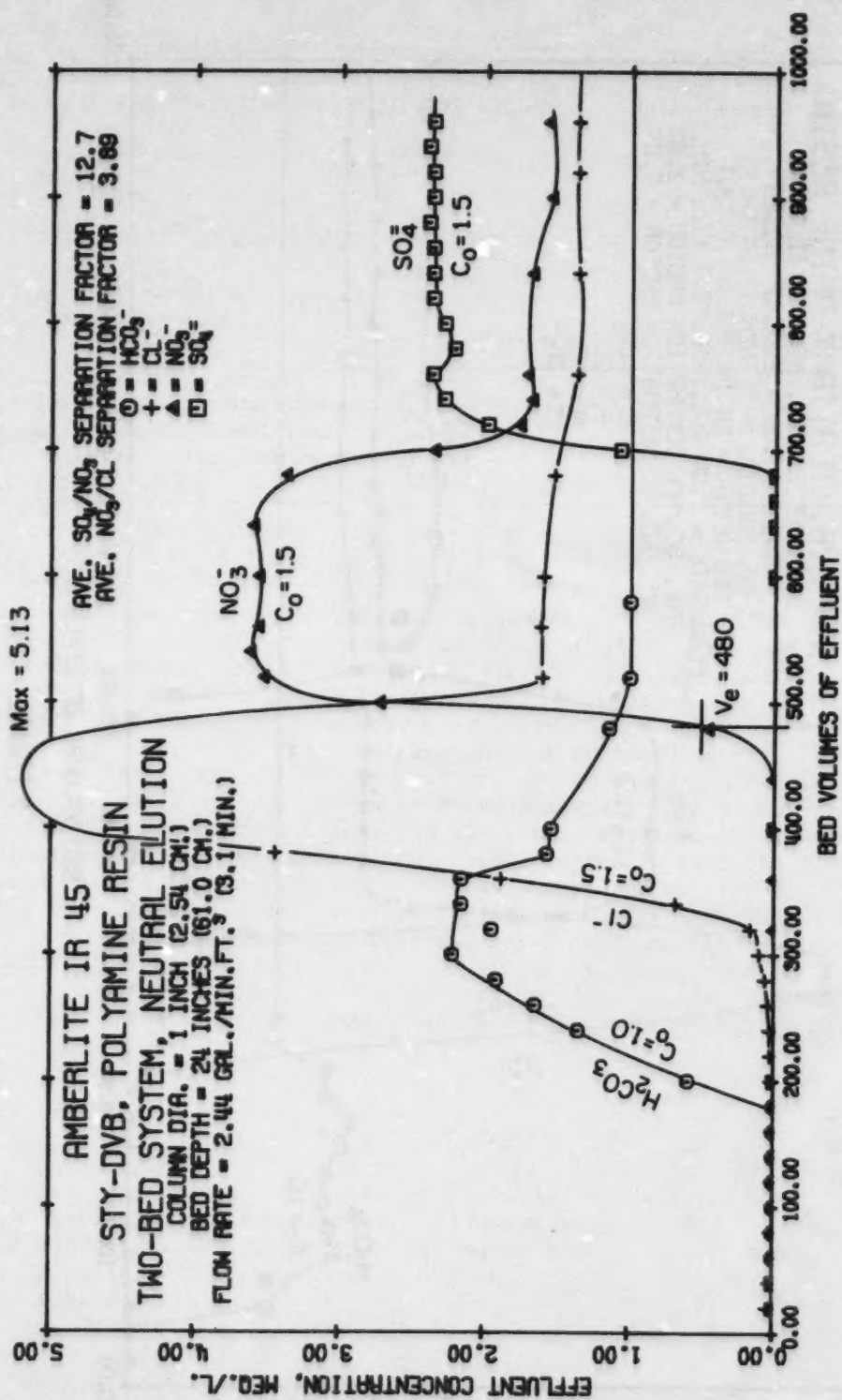


FIGURE C11
RUN NO. 11, EFFLUENT CONCENTRATION PROFILE

APPENDIX D

EXPERIMENTAL APPARATUS AND PROCEDURES

TABLE D1.
U.S. ION EXCHANGE RESIN MANUFACTURERS

Manufacturer	Trade Name
Dow Chemical Company Functional Products and Systems Dept. Midland, Michigan 48640	Dowex Resins
Diamond Shamrock Chemical Co. Noplo Chemical Division 1901 Spring St. Redwood City, CA 94063	Duolite Resins
Ionac Division of Sybron Corp. Dirmingham, New Jersey 08011	Ionac Resins
Rhom and Haas Company Fluid Process Chemicals Dept. Philadelphia, PA 19105	Amberlite Resins

NOTES: A complete list (1967) of World-Wide "Producers of Ion-Exchange Materials" can be found on p. 85 of: Operation and Control of Ion-Exchange Processes for Treatment of Radioactive Wastes" Reference 68.

Other descriptions and sources of ion exchangers are listed in the appendices of Dorfner's Ion-Exchangers (1972), Reference 40, and Helfferich's Ion Exchange

(1962) Reference 60.

TABLE D2.
CHEMICAL MAKE-UP OF Na TEST WATER
(See Also Table 20)

* Chemical	Formula Weight	$\frac{\text{m moles}}{\ell}$	$\frac{\text{gms}}{100 \ell}$
NaHCO_3	84.01	1.00	8.401
NaNO_3	84.99	1.50	12.75
Na_2SO_4	142.0	0.75	10.65
NaCl	58.44	1.50	8.77

TABLE D3.
CHEMICAL MAKE-UP OF Ca-Mg-Fe TEST WATER
(See Also Table 21)

* Chemical	Formula Weight	$\frac{\text{m moles}}{\ell}$	$\frac{\text{gms}}{100 \ell}$	Order of Addition
NaHCO_3	84.01	1.00	8.401	1
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	236.15	0.75	17.71	2
MgSO_4	120.37	0.75	9.03	3
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	147.03	0.75	11.03	4
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	278.03	1 ppm Fe	0.500	5

* Dissolve weighed salt in small quantity of distilled water (approximately 1 ℓ) before adding to 100 ℓ batch.

D1: PROCEDURE FOR RESIN CONDITIONING

- 1) Place 500 ml or 1000 ml weak base resin sample in free base form into 51 cm I.D. resin conditioning column (Figure D1).
- 2) Backwash with tap water at 100% or greater bed expansion for 5-30 minutes or until effluent appears clear and colorless.
- 3) Exhaust resin sample downflow with 2-3 BV of 2.0 N HCl during a 30-45 minute period; flow rate $\approx$ 70 ml/min for the 1 ℓ

resin samples.

- 4) Rinse downflow with 4-6 BV of distilled water for a total rinse contact time of about 30 minutes; flow rate $\approx$ 130 ml/min for 1 l resin samples.
- 5) Regenerate downflow with 2-3 BV of 1.5 N NaOH during a 30-45 minute contact time; flow rate $\approx$ 70 ml/min for 1 l of resin.
- 6) Repeat step 4: distilled water rinse.
- 7) Repeat step 3: exhaustion with HCl.
- 8) Repeat step 4: distilled water rinse.
- 9) Repeat step 5: regeneration with NaOH.
- 10) Repeat step 4: distilled water rinse.
- 11) Drain column till water level is about 8 cm above resin level.
- 12) Slurry the resin by rocking the stoppered column, then transfer resin-water slurry to polyethylene bucket by multiple rinsing of inverted column.
- 13) Decant supernatant distilled water and any floating beads or debris then return wet resin slurry to original container.
- 14) Place 100 ml of wet resin slurry into 350 ml EC fitted glass funnel on 1000 ml vacuum flask.
- 15) Rinse three times with about 60 ml of distilled water each time then wash continuously with a stream of about 50 ml of distilled water from squirt bottle.
- 16) Draw air thru resin for about 2 minutes.
- 17) Transfer damp resin to polyethylene tray and air dry for about 3-5 days at 25° C in walk-in incubator at about 50% relative humidity.

NOTES: a) For strong-base resins in the chloride form and strong-acid resins in the Hydrogen form, the sequence of acid-base addition is reversed.
b) A total of six columns were used.
c) This procedure was carried out on 32 anion resin samples and 4 cation resin samples. All resins used for experiments were conditioned by this procedure.

D2: RESIN CONVERSION PROCEDURE

Objective: to convert the free base form of a weak base resin to the nitrate form at .005 N equilibration concentration.

- 1) Assemble resin conversion apparatus as in Figure D2 .
- 2) Place about 75 ml of wet, free-base form, weak-base anion resin into 21 mm. I.D. glass ion-exchange column.
- 3) Backwash resin with tap water and allow to settle. Drain water to a level about 1 cm above resin bed.
- 4) Pass 400% stoichiometric excess (about 300 ml) of 2 N. HNO_3 through the resin at about 1 gal/min ft^3 ($\tau = 7.5$ min) for a total contact time of about 45 minutes.

5) Rinse with 10 BV (750 ml) of .00500 N. HNO_3 at about 20 ml/min.

6) Allow resin to equilibrate with .00500 N. HNO_3 overnight in the column.

7) Remove resin from column, filter on glass frit into vacuum flask. Draw air through resin for about 1 min. after washing resin with a stream of about 50 ml of .00500 N. HNO_3 from a wash bottle.

8) Rinse quickly with two separate, one BV quantities of 0.001 N. HNO_3 to remove adhering .00500 N. HNO_3 .

9) Draw air through resin for about one minute.

10) Transfer dry, caked resin from filter to polyethylene pan and air dry in walkin incubator for 2-4 days at ambient humidity and 25° C.

11) Store air-dried, nitrate form resin in 4 oz. wide-mouth polyethylene bottles for use in isotherm experiments and capacity determinations.

NOTES: a) This same procedure was used to prepare Chloride and Sulfate form resins at .00200, .00500 and .00800 N. with those acid and those concentrations being substituted where appropriate in the procedure above. In all cases the initial conversion was done with 2N acid and the final, fast rinse was done with 0.001 N. acid.

b) a total of six columns were constructed and typically 6 resins were converted simultaneously.

D3: PROCEDURE FOR EQUILIBRIUM ISOTHERM CONSTRUCTION

Objectives: To obtain experimental data at 25° C so that sulfate/nitrate and chloride/nitrate equilibrium isotherms might be developed for all the anion resins.

To obtain at least five equally distributed equilibrium points for each isotherm at a total solution concentration of 0.005 N.

Note: The example discussed here is for the construction of a sulfate/nitrate isotherm starting with a resin in the nitrate form (see Procedure D2) which is placed into 0.005 N H_2SO_4 for equilibration.

1) Estimate the grams of resin in the nitrate form which must be added to 100 ml aliquots of 0.005 N H_2SO_4 to achieve equilibrium sulfate concentrations (x_s 's) approximately equal to 0.1, 0.3, 0.5, 0.7, and 0.9. To accomplish this, the ion-exchange capacity and the separation factors for sulfate/nitrate exchange must be known or estimated. In this work, the capacities were known from measurements and published data, and the separation factors were estimated (but the original estimates were not very good in many cases). Equation E10 (from Appendix

E, Example Calculation E1) is then used to calculate the resin weights required for each equilibrium point.

2) Add the calculated amounts of resin to the 100 ml aliquots of H_2SO_4 in 125 ml French-square bottles and tumble at 13 rpm for 24 hours at 25° C.

3) Analyze the equilibrated supernatants for sulfate and nitrate using Procedures D7 and D8 of this Appendix.

4) Using the predetermined nitrate capacity of the resin, calculate the meq of nitrate remaining on the resin at equilibrium.

5) Calculate the meq of sulfate on the resin by measuring the disappearance of sulfate from the liquid phase.

6) Knowing the meq of sulfate and nitrate in both phases, calculate the equilibrium equivalent fractions of each of the ions in each phase.

7) Construct the isotherms by plotting y_s vs x_s for each equilibrium point for a given resin. See Appendix A Figures A1--A32.

Notes: Because there were so many data points, a HP-25 Programmable calculator was used to calculate the x_i 's and y_i 's and separation factors from the experimental data. Because the equilibrium data were to be used for several data plots, they were stored in an MTS computer file for use in generation of the isotherm plots: Text Figures 12--17 and Appendix Figures A1--A32. Alternatively, resins in the sulfate form previously equilibrated with 0.005 N H_2SO_4 may be used with 0.005 N HNO_3 solution to construct the same isotherms. This procedure was followed for construction of the lower hysteresis isotherm shown in Figure 18.

The procedures above are essentially the same for the construction of the chloride/nitrate isotherms, but HCl is substituted for H_2SO_4 .

D4: BICARBONATE SELECTIVITY DETERMINATION PROCEDURE

Objectives: To determine the carbonic acid/nitric acid selectivities of a representative number of anion resins;
To determine if a significant amount of H_2CO_3 is taken up at low pH (2.5 - 3.0) by weak and strong base resins.

1) Weigh out 1.00 meq of resins in the Chloride form using the experimentally determined capacities in meq/gm of air-dried resin.

2) Transfer weighed resins to the mini columns (figure D1) filled with distilled water.

3) Assemble mini columns into the apparatus as shown in Figure D4. The cation column contained 120 ml of Duolite C-20 resin in the hydrogen form with an approximate capacity of 240

meq. A 16 liter reservoir of feed solution at a total concentration of 5 meq/l (80 meq total), not shown in the photo, is used to gravity feed the system. Five different feed solution mixtures of sodium nitrate and sodium bicarbonate were used having the following equivalent fractions of nitrate and bicarbonate:

Feed Solution Label	X_{HCO_3}	X_{NO_3}
.1	.1	.9
.3	.3	.7
.5	.5	.5
.7	.7	.3
.9	.9	.1

4) Pass approximately 1 l of cation effluent through each of the mini columns at a rate of about 5-6 ml/min. This provides a 400% stiochiometric excess and an exposure time of about 2 1/2 hours.

5) Drain the column down to the top of the resin.

6) Remove mini-columns from apparatus and regenerate by adding 5 ml of 2% NH_4OH (0.57 meq/ml) to each column using care not to mix the resin and regenerant (Use 0.5 N. NaOH for strong-base resins).

7) Drip this slowly through the column for 15-20 minutes, i.e. about 1 ml/4 min., into a 100 ml volumetric flask 1/2 filled with distilled water.

8) Repeat step 6.

9) Repeat step 7.

10) Rinse slowly with about 5 ml of distilled water over a 10 min. period.

11) Repeat step 10.

12) Rinse quickly, pinch clamp opened wide, with 5 ml of distilled water.

13) Repeat step 12.

14) Repeat step 12.

15) Make up to 100 ml with distilled water.

16) Repeat steps 1-15 for each of the five feed solutions listed in step 3.

17) Analyze for nitrate by the UV method which has been demonstrated by experiment to be free from interferences from all the anions and cations present in these regenerant solutions.

18) Analyze for bicarbonate using the inorganic carbon channel of the Beckman TOC analyzer using 100 microliter samples.

NOTES: a) Weak base resins 1-6 & 8-10 and strong-base resins 16, 19 and 21 were analyzed in this fashion. Very little H_2CO_3 was taken up even at 0.9 equivalent fraction of HCO_3^- in feed. The range of H_2CO_3 uptake was 2-5% of the total resin capacity or this pH (2.4-3.0).

b) A definite kinetic effect was noted; H_2CO_3 did promote the uptake of HNO_3 . For example the resins went from typi-

cally 70% of total capacity utilized at $X_B = .1$, $X_N = .9$ to 100% utilized at $X_B = .3$, $X_N = .7$ with no significant increase in H_2CO_3 uptake. Apparently it takes an equivalent fraction of HCO_3^- greater than 0.10 to facilitate the stoichiometric uptake of HNO_3 under these conditions.

D5: TITRATION CURVE DETERMINATION PROCEDURE

Objectives: To establish titration curves for HCl , HNO_3 and H_2SO_4 for each of the weak-base anion resins: these curves to be used later in the analysis of selectivity data and to help model resin behavior in fixed bed processes.

To determine the pK_a 's of each of these resins. To compare the capacities of each for Chloride, Nitrate and Sulfate as a function of pH.

1) Prepare the following standard acids and check by titration with 1.000 NaOH to pH 7.0 and 4.5. Standardize to 4 significant figures.

1.000 N. HCl

1.000 N. HNO_3

1.000 N. H_2SO_4

2) Weigh out 500 mg (+2 mg) of air-dried free-base form resin into 125 ml, square, glass, wide-mouth bottles: forty-two separate weighings for each different resin.

3) Into each of the above bottles place one of the following amounts of standardized HCl , HNO_3 , or H_2SO_4 .

<u>Bottle No.</u>	<u>Meq of Acid</u>	<u>Ml of Dist. H_2O</u>
1	0.0	100
2	0.30	100
3	0.70	99.0
4	1.10	99.0
5	1.40	98.5
6	1.60	98.5
7	1.80	98.0
8	2.00	98.0
9	2.20	98.0
10	2.40	97.5
11	2.60	97.5
12	2.90	97.0
13	3.30	97.0
14	3.70	96.0

4) Place bottles into tumbler (Figure D3) and rotate for 16 to 24 hours at 13 rpm.

5) Measure and record pH of equilibrated samples using potentiometric, strip-chart recorder to determine when pH reading has stabilized. Do not rinse electrode with water between samples; simply touch a Kimwipe to the bottom of the com-

bination electrode to absorb adhering sample before immersion into new sample.

6) Determine density of air-dried, free-base form resin by weighing 3.500 gm into glass bottle, adding 100 ml distilled water, tumbling overnight and measuring volume in 10 ml graduate after light tamping and settling for 10 minutes.

7) Plot pH vs meq acid added and pH vs meq/ml of resin. See Figures B1 thru B13.

8) Determine capacities at any pH by assuming H^+ ion activity = H^+ concentration in 100 ml liquid; and H^+ ion added, but not in liquid, is in solid phase (resin). See Table B1 for resin capacity comparisons.

NOTES: a) Duolite ES-368 floats and adheres to pH electrode.
b) Densities of Chloride forms of strong base resins were determined as in step 6 except 3.00 gm resin used.

D6: HCl CAPACITY DETERMINATION PROCEDURE

(Generally the same procedure is used for HNO_3 and H_2SO_4 Capacity)

1) Into Al weighing dishes⁴ weigh out duplicate 0.600 gm (+1 mg) air-dried, Chloride form of resins previously equilibrated with .00500 N HCl.

2) Quantitatively transfer the weighed resin samples into mini-columns (Figure D1) and cover with distilled water.

3) Carefully add 10 ml of 2 N. HNO_3 to the column and drip slowly through resin (total contact time³ of 15 to 30 minutes) collecting the HNO_3 in a beaker.

4) Repeat step 3 collecting the regenerant HNO_3 in the same beaker.

5) Rinse quickly with 10 ml of .005 N. HNO_3 collecting rinse in same beaker.

6) Repeat step 5 with another 10 ml of 0.005 N. HNO_3 .

7) Rinse quickly with 10 ml of distilled water into same beaker.

8) Titrate the total regenerant volume including rinses with standardized 0.100 N. $AgNO_3$ to + 290 mV end point with Fisher Automatic Titrator using³ double junction calomel reference electrode and Ag/AgS specific ion electrode. See Potentiometric Titration Method for Chloride for full details.

NOTES: a) Blank for step 8 = 20 ml of 2N. HNO_3 + 20 ml of .005 N. HNO_3 + 10 ml of distilled water.
b) Standard = 20 ml of 2 N. HNO_3 + 20 ml of .005 N. HNO_3 + 10 ml distilled water + 4.00 ml³ of 1.000 N. NaCl.
c) To determine HNO_3 capacity, start with air-dried, nitrate form and elute with HCl. Dilute and analyze for nitrate by UV method.
d) To determine H_2SO_4 capacity, start with air-dried, sulfate form resins² and elute with HCl. Dilute and analyze for sulfate by modified turbidimetric method.

D7: MODIFIED TURBIDIMETRIC METHOD FOR SULFATE

Reference: Standard Methods, 13th Ed., p. 334

- 1) Place 100 ml sample in 300 ml Erlenmeyer flask.
- 2) Add 5 ml conditioning reagent.
- 3) Add one "scoop" (0.2 - 0.3 ml) of reagent grade barium chloride.
- 4) Shake by hand swirling occasionally for one minute.
- 5) Allow 4 additional minutes for turbidity to develop with no additional agitation.
- 6) Set 10 ppm sulfate to read "100" on 0-100 scale of Hach turbidimeter (Model 2100A) using 25 ml sample and no spacer in the reading chamber.
- 7) Read turbidity of all standards and samples after exactly 4 minutes of turbidity development following initial 1 minute agitation period.
- 8) Plot NTU vs ppm sulfate and read off samples
Typically, $\text{ppm} = 1.0 + 0.09 \text{ NTU}$

- NOTES:
- a) Linear range is 2-10 ppm sulfate.
 - b) Standards typically 2, 4, 6, 8, and 10 ppm sulfate.
 - c) Method described in Std. Methods was quite time-consuming, insensitive, and didn't give reproducible results presumably because light absorption rather than reflected light was being measured.
 - d) See Std. Methods for preparation of reagents and standards.

D8: ANALYTICAL METHOD FOR NITRATE BY UV ABSORPTION

Reference: Standard Methods, 13th Ed., p. 237

- 1) To 50 ml sample add 1.00 ml of 1.0 N. HCl.
- 2) Using square, 1 cm, silica cuvetts measure absorbance at 220 nm. Do this for all standards and samples before changing wavelength setting on UV-VIS spectrophotometer.
- 3) Measure absorbance at 275 nm.
- 4) Calculate ppm nitrate concentration from calibration curve plotted using corrected absorbance: Abs_{corr}

$$\text{Abs}_{\text{corr}} = \text{Abs}_{220} - 2 (\text{Abs}_{275})$$

$$\text{Typically, ppm} = 4.00 \text{ Abs}_{\text{corr}}$$

- NOTES:
- a) Linear range is 1-4 ppm nitrate.
 - b) Standards of 1 and 3 ppm usually run.
 - c) Set zero on spectrophotometer using distilled water blank with acid added.
 - d) Use same cuvet for all measurements in single beam spectrophotometer.
 - e) In every experiment the effects of possible interferences was checked. Where organic extractables from the

resins were high, nitrate was also high and dilution eliminated serious interference.

D9: POTENTIOMETRIC TITRATION METHOD FOR CHLORIDE

Reference: None; method developed here and possible interferences checked out.

- 1) Make sample to be titrated up to approximately 50 ml in a 150 ml beaker with teflon-coated magnetic stirring bar.
- 2) Titrate with 0.0141 N. AgNO_3 (.500 meq Cl/ml) using Fisher Automatic Titrimeter to + 290 mV end point. This was previously determined to coincide with the inflection point in the ml titrant added vs mV plot. Potential due to increase in Ag^+ ion was measured using double junction (nitrate-external) calomel, reference electrode (Orion 90-02-00) with Ag/AgS solid state specific ion electrode (Orion 94-16A).

- NOTES:
- a) Sensitivity is 125 mV/ml titrant added at inflection point for .0141 N. AgNO_3 .
 - b) AgNO_3 standardized against 1000 ppm NaCl.
 - c) For concentrated chloride solutions use 0.100 N. AgNO_3 .
 - d) It is optional but not necessary to acidify with 5 ml of 1:1 HNO_3 if pH is below 7.
 - e) This method was used for all capacity determinations and isotherm determinations. Chloride in column effluents was determined by combination chloride electrode (Orion 96-17).

D10: CARBONIC ACID AND BICARBONATE DETERMINATIONS

Reference: For Instrument operations: Beckman Model 915 Total Organic Carbon Analyzer Instruction Manual

Objective: To determine H_2CO_3 (dissolved but volatile CO_2) in acidic ion-exchange column effluents and HCO_3^- or $\text{CO}_3^{=}$ in neutral to basic effluents.

- 1) Withdraw 100 microliter sample of column effluent directly from flowing effluent stream by submerging syringe tip 4 cm below surface in overflowing 100 ml beaker in which effluent tube is submerged. Rinse syringe at least twice by discharging contents anywhere except back into beaker. Draw sample up slowly to avoid CO_2 bubbles.
- 2) Inject into inorganic channel of TOC analyzer previously standardized with Na_2CO_3 or NaHCO_3 (freshly prepared and kept stoppered).
- 3) Make at least duplicate injections or repeat until reproducible peaks are obtained.
- 4) From peak height, determine mm/l CO_2 evolved.

NOTES: a) Peak height vs concentration curve is approximately

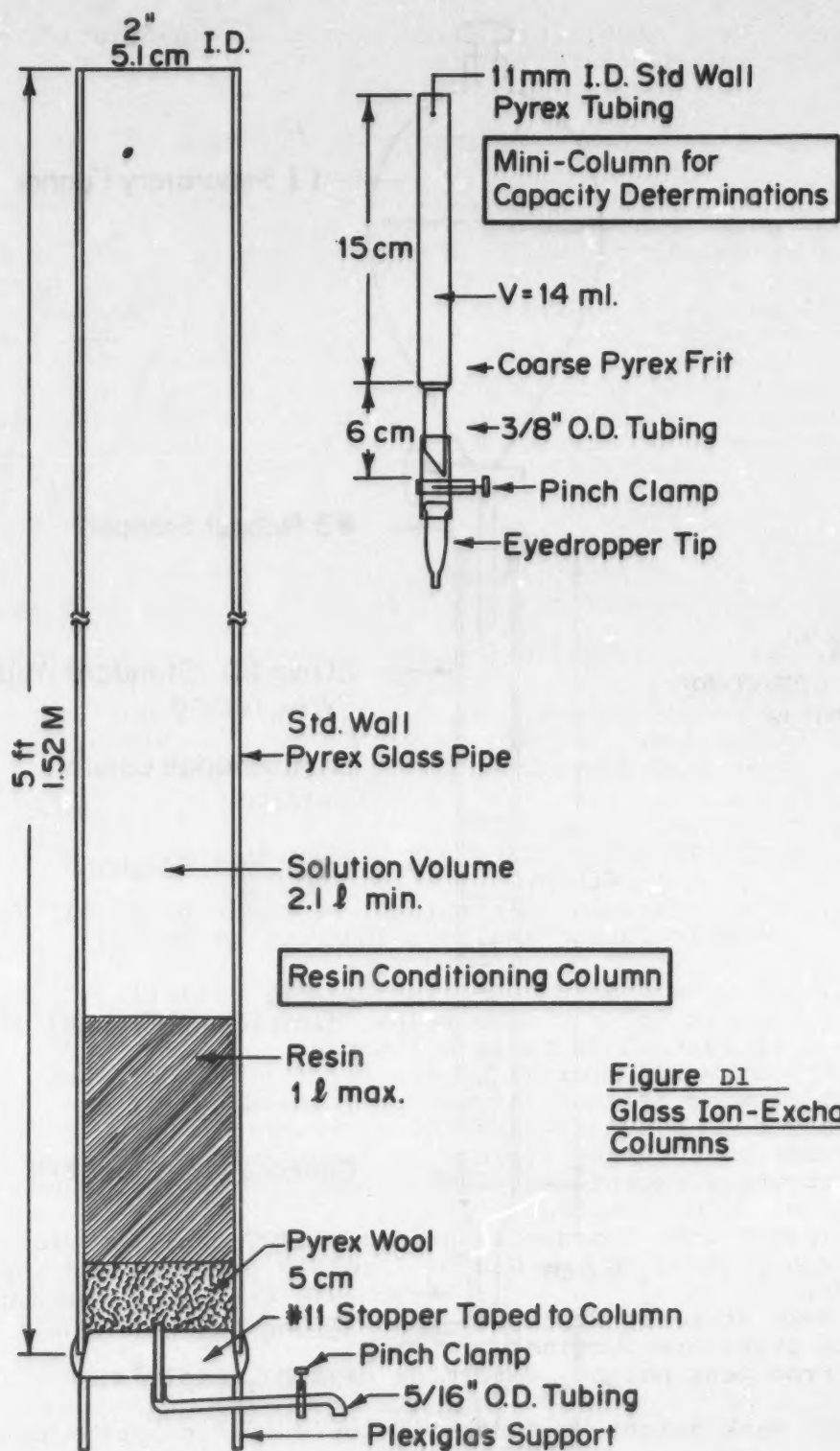
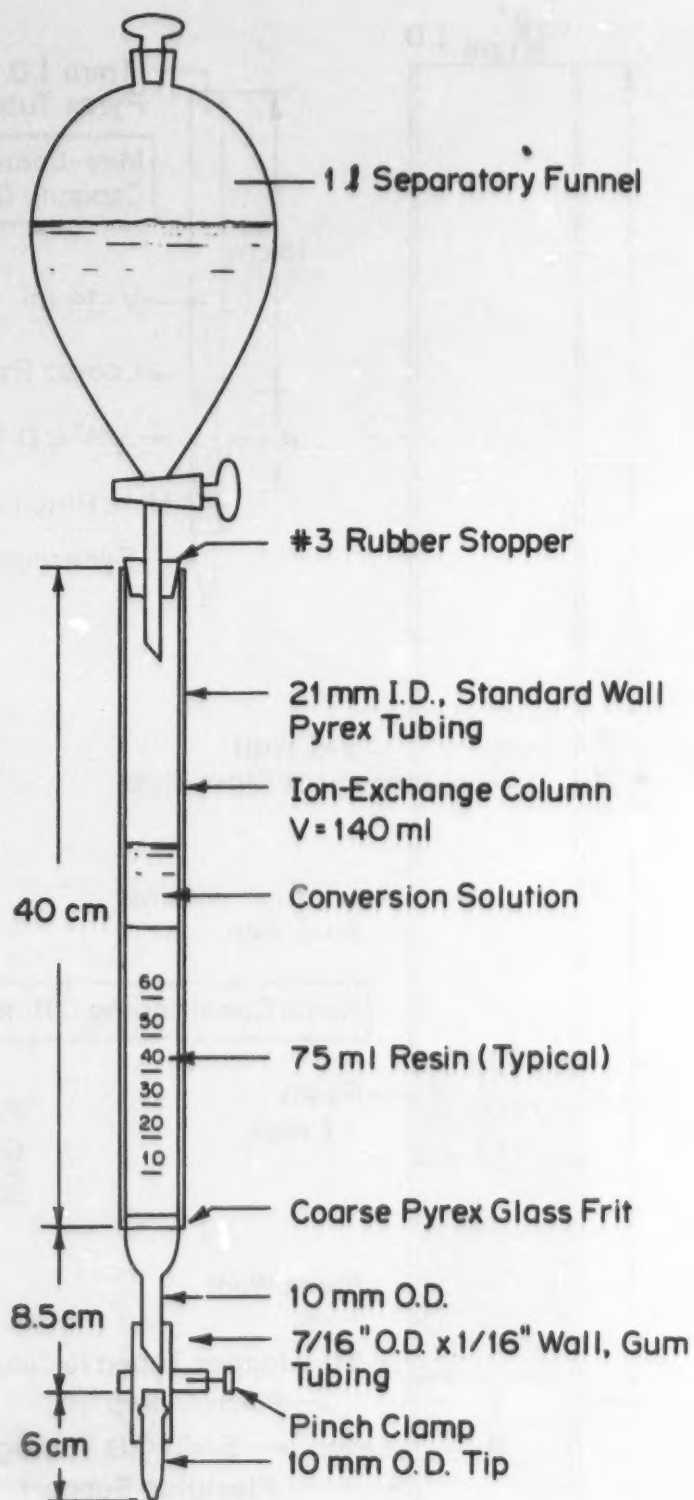


Figure D1
Glass Ion-Exchange
Columns

Figure D2
Resin Conversion
Apparatus



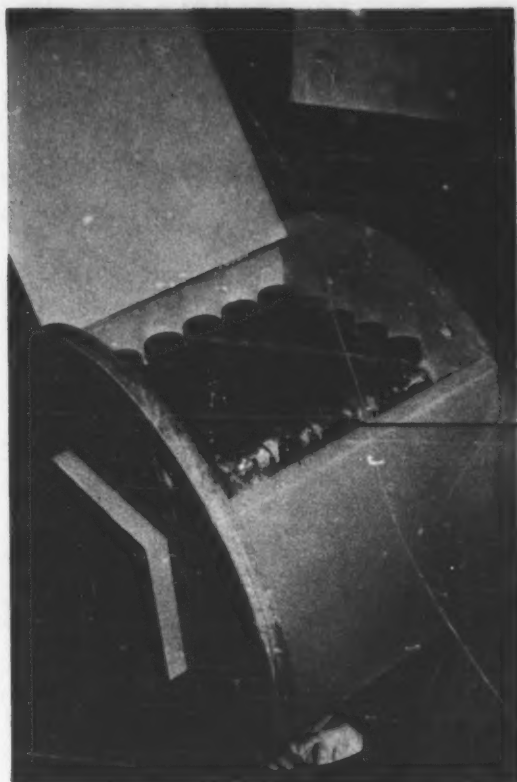
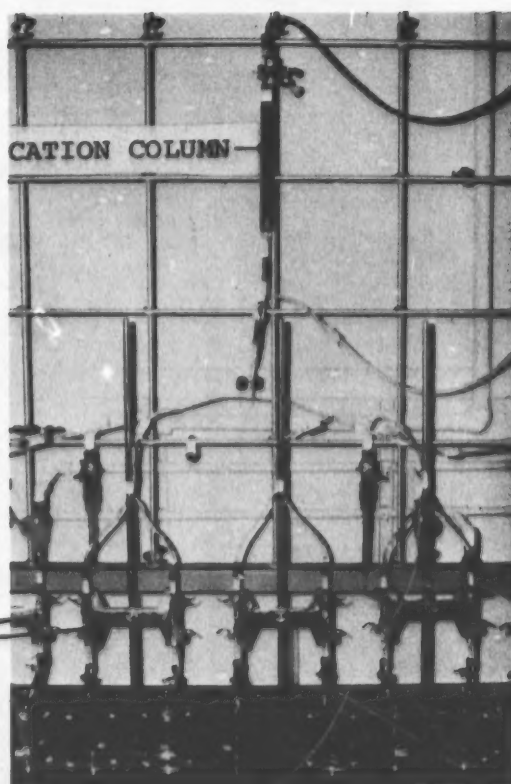
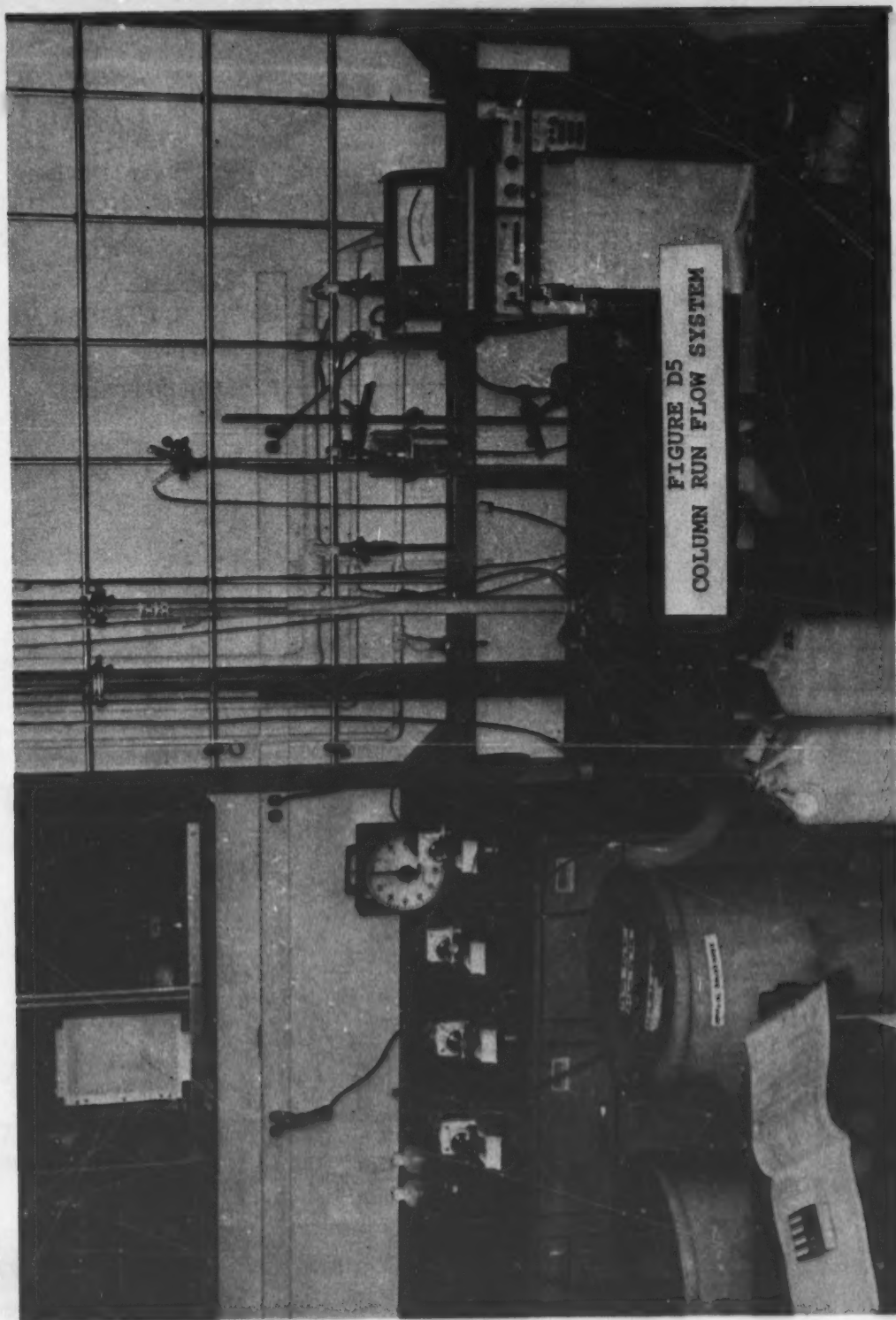


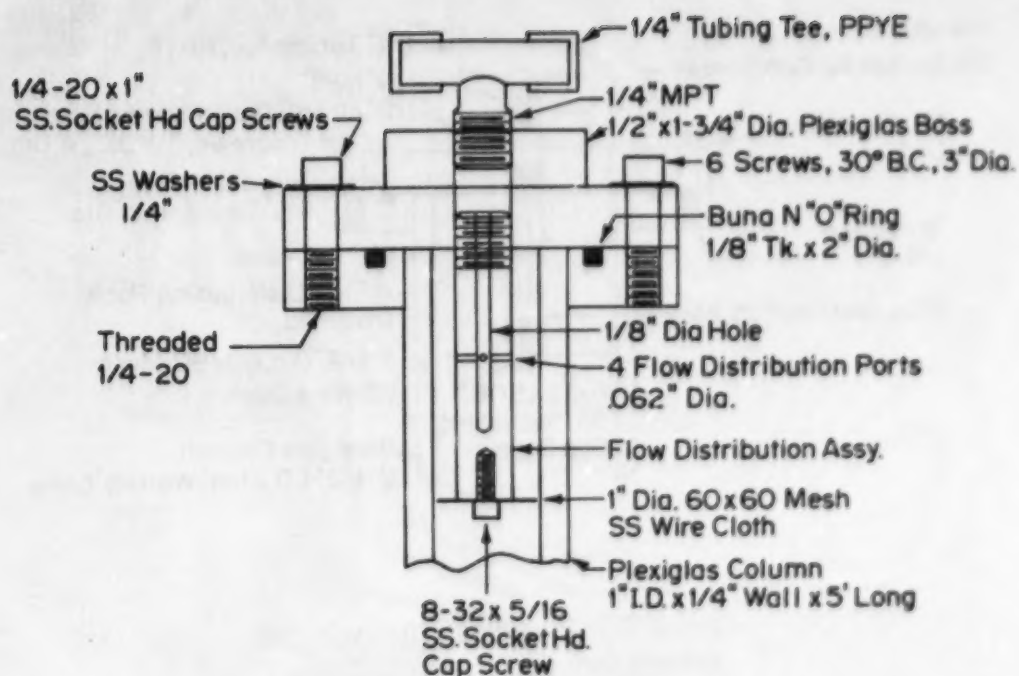
Figure D3
ISOTHERM TUMBLER
WITH
125 ML BOTTLES

FIGURE D4
BICARBONATE SELECTIVITY
APPARTUS



ANION MINI-COLUMNS

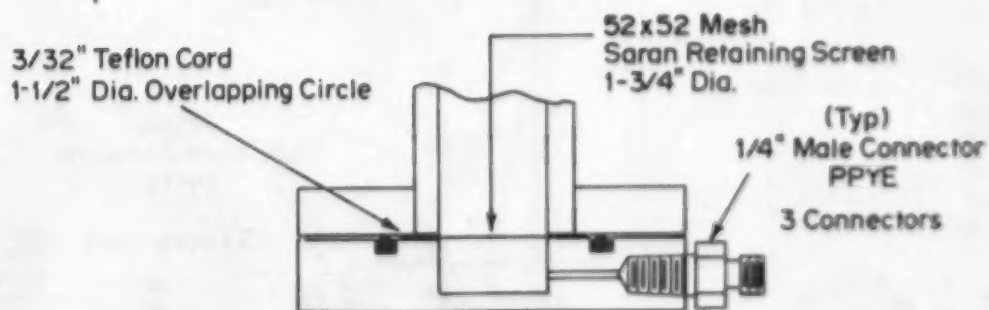


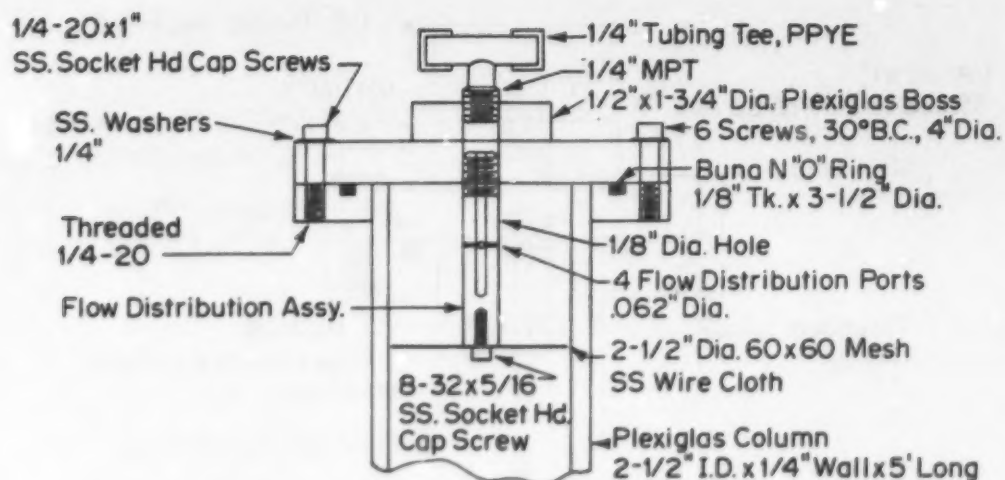


1" Dia. Plexiglas Ion-Exchange Column Details

FIGURE D6

1" Dia. Plexiglas Ion Exchange Column Details

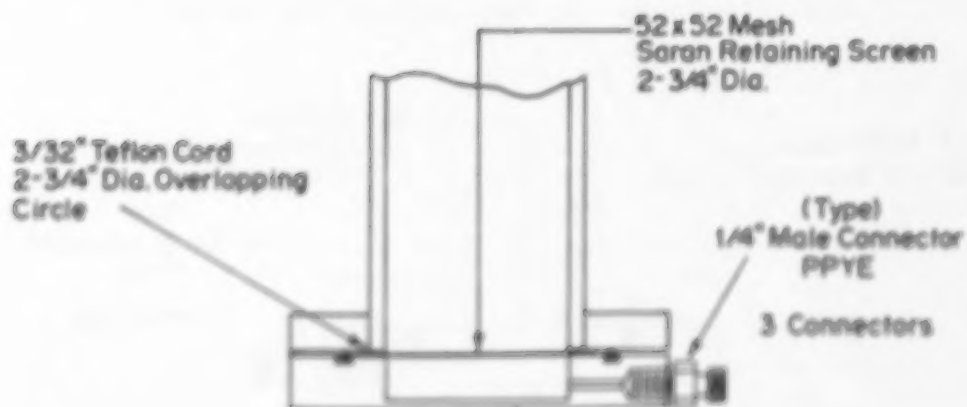




2-1/2" Dia. Plexiglas Ion-Exchange
Column Details

FIGURE D7

2 1/2" Dia. Plexiglas Ion-Exchange Column Details



linear in 0-2 mm/l range.

b) Reproducibility at 1 mm/l was + 2%.

c) Typical standards were 0.5, 1.0, 1.5 and 2.0 mm/l.

mm/l = millimoles/l

APPENDIX E

CALCULATIONS AND DERIVATIONS

Find $\beta = \frac{\text{gms Resin}}{\text{mm/l}}$; Given x_A , α_B^A , A_0 , $\bar{B}_0$

E1: EXAMPLE CALCULATION FOR BINARY ION EXCHANGE ISOTHERM

Objective: To determine the wt. of Resin (W , gms) containing only counterions "B" at conc. $\bar{B}_0$ meq/gm which should be added to a given Volume (V , liters) of solution containing only counterions "A" at a conc. A , meq/l to produce the desired equilibrium equivalent fraction of A, i.e., x_A .

Also Solve for $x_A = f(\alpha, \beta, A_0, \bar{B}_0)$

Given the following constraints on the Equilibration Process.

- (a) Constant total concentration in the liquid phase; i.e. A_0 = Total initial Conc. of A = C_T total liquid phase conc. -- final and initial

$$A_0 + B_0 = C_T; A_0 = C_T \text{ when } B_0 = 0$$

$$A + B = C_T = A_0$$

Dividing by: C_T or A_0 (E1)

$$x_A + x_B = 1$$

- (b) Constant total concentration in the solid phase; i.e. $\bar{B}_0$ = total initial conc. of B on resin = Q , the constant capacity of the resin

$$\bar{A} + \bar{B} = Q$$

$$\bar{A}_0 + \bar{B}_0 = Q; \bar{B}_0 = Q \text{ when } \bar{A}_0 = 0$$

Dividing by: Q or $\bar{B}_0$ (E2)

$$y_A + y_B = 1$$

- (c) Constant separation factor: α_B^A , an approximation

$$\alpha_B^A = \frac{y_A x_B}{x_A y_B} \quad (E3)$$

(d) Mass balance on A, i.e. liquid phase loss of A = Solid phase gain of A.

$$V (A_0 - A) = W \bar{A} \quad (E4)$$

where: A, B = Conc. in liquid phase (meq/l)

$\bar{A}, \bar{B}$ = Conc. in solid phase (meq/gm)

$A_0, B_0, \bar{A}_0, \bar{B}_0$ = Initial concentrations (meq/l; meq/gm)

$C_T, \bar{C}_T$ = Total concentrations (meq/l, meq/gm)

x_A, x_B = Equivalent Fractions, Liquid Phase

y_A, y_B = Equivalent Fractions, solid phase

V = Volume of liquid phase (l)

W = Weight of Resin (gms)

$\beta = W/V$ (gms of resin/l)

Q = Resin capacity (meq/gm)

$\alpha = \alpha_B^A$ = Separation Factor (Dimensionless)

Solution:

from (2) and (4), where $C_T = A_0, \bar{C}_T = \bar{B}_0$

$$\text{and } \frac{V}{A_0 B_0} (A_0 - A) = \frac{W}{A_0 B_0} \bar{A}$$

$$\frac{V}{B_0} (1 - x_A) = \frac{W}{A_0} y_A$$

$$y_A = \frac{1}{\beta} \frac{A_0}{B_0} (1 - x_A) \quad (E5)$$

from (2) $x_B = 1 - x_A$

from (2) and (5)

$$y_B = 1 - y_A$$

$$y_B = 1 - \frac{A_0}{\beta B_0} (1 - x_A) \quad (E6)$$

from (3), (5), (2) and (6)

$$\alpha_B^A = \frac{\frac{A_0}{\beta B_0} (1 - x_A) (1 - x_A)}{x_A \left(1 - \frac{A_0}{\beta B_0} (1 - x_A) \right)}$$

$$\alpha_B^A = \frac{\left(\frac{A_0}{B_0}\right) (1 - x_A) (1 - x_A)}{\beta x_A - \frac{A_0}{B_0} x_A (1 - x_A)} \quad (E7)$$

In std. Quadratic form:

$$\frac{\alpha \beta \bar{B}_0}{A_0} x_A - \alpha x_A \frac{A_0 \bar{B}_0}{B_0 A_0} (1 - x_A) = 1 - 2x_A + x_A^2 \quad (E8)$$

$$\frac{\alpha \beta \bar{B}_0}{A_0} x_A - \alpha x_A + \alpha x_A^2 - 1 + 2x_A - x_A^2 = 0$$

$$\boxed{(\alpha - 1)x_A^2 + \left(\frac{\alpha \beta \bar{B}_0}{A_0} - \alpha + 2\right)x_A - 1 = 0} \quad (E9)$$

Solving [8] for β , the Desired ratio of gms. resin/l solution

$$\frac{\alpha \bar{B}_0}{A_0} \beta x_A = x_A^2 - \alpha x_A^2 - \alpha x_A - 2x_A + 1$$

$$\boxed{\beta = \frac{(1 - \alpha)x_A^2 + (\alpha - 2)x_A^2 + 1}{\frac{\alpha \bar{B}_0}{A_0} x_A}} \quad (E10)$$

Example problem: Find the amounts of resin in NO_3 form to add to a solution of 0.005 N. H_2SO_4 that an equivalent isotherm might be developed with 5 Data points.

(a) Given: Resin originally in NO_3 Form

$$A_0 = C_T = 0.005 \text{ N.} = 5.00 \text{ meq/l } \text{H}_2\text{SO}_4$$

$$B_0 = Q = \bar{C}_T = 3.39 \text{ meq/gm } \text{HNO}_3$$

$$\alpha_B^A = \alpha_{\text{NO}_3}^{\text{SO}_4} = 2.50 \text{ AN ESTIMATE!}$$

Solution: Generate a table of β values x_A values using equation (10)

$x_A = x_{SO_4}$	Calculated β	
0.1	6.1062	} gms of resin in the NO_3 form (previously equilibrated with .005 N. HNO_3) to be added to 1 l of 0.005 N. H_2SO_4 to achieve equilibrium at approximately the x_A (i.e. x_{SO_4}) values shown.
0.3	1.9961	
0.5	1.0324	
0.7	0.5183	
0.9	0.1540	

(b) Given: Resin originally in the SO_4 form

$$A_0 = C_T = 0.005 \text{ N. } HNO_3 = 5 \text{ meq/l}$$

$$\bar{B}_0 = C_T = Q = 3.39 \text{ meq } H_2SO_4/\text{gm}$$

$$\alpha_B^A = \alpha_{SO_4}^{NO_3} = 0.400 \text{ SAME ESTIMATE AS IN PART (a)}$$

Solution: Generate table as in part (a) using eq. (10)

$x_A = x_{NO_3}$	Calculated β	
0.1	31.1947	} gms of resin in the SO_4 form (previously equilibrated with 0.005 N. H_2SO_4) to be added to 1 l of 0.005 N. HNO_3 to achieve equilibrium at approximately the x_A (i.e. x_{NO_3}) values shown.
0.3	7.0551	
0.5	2.58	
0.7	0.9166	
0.9	0.1885	

E3: DERIVATION AND JUSTIFICATION OF α_j^i

Ratio of Isotherm Areas Related to Separation Factor

$$R_a = f(\alpha)$$

Objectives: To mathematically relate the ratio (R_a) of the area below the isotherm to that above the isotherm to the separation factor (α). That relationship will be used to determine the best fit, averaged α given the measured areas below and above the experimentally determined isotherm. To justify the use of the separation factor α as opposed to the selectivity coefficient as a measure of the resin phase preference of one ion over another.

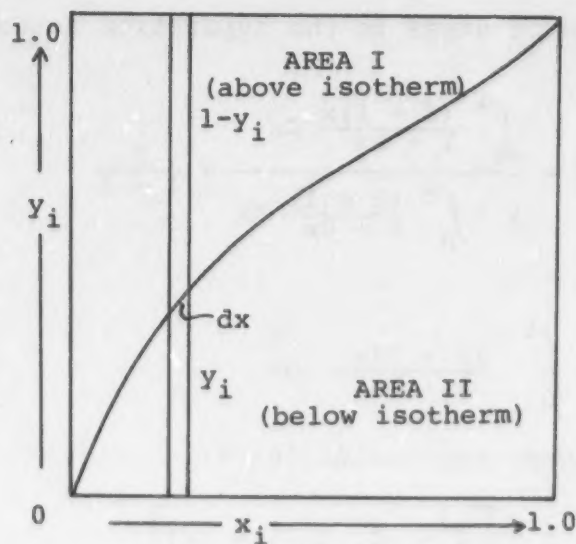


FIGURE E1
Example Isotherm

Definition of separation factor: α_j^i

$$\alpha_j^i = \frac{y_i}{x_i} / \frac{y_j}{x_j} = \frac{y_i(1 - x_i)}{(1 - y_i)(x_i)}$$

Dropping subscripts and rearranging:

$$y = \frac{ax}{1 - x + ax} = \frac{ax}{1 + (a - 1)x}$$

Let $\beta = a - 1$, then $a = \beta + 1$

$$y = \frac{(\beta + 1)x}{1 + \beta x}$$

$$\text{Area II} = \int_0^1 y dx$$

$$\text{Area I} = \int_0^1 (1 - y) dx$$

Relating the ratio of areas to the separation factor

$$\frac{\text{Area II}}{\text{Area I}} = \frac{\int_0^1 \frac{(\beta + 1)x}{1 + \beta x} dx}{1 - \int_0^1 \frac{(\beta + 1)}{1 + \beta x} dx} = \frac{Z}{1 - Z}$$

where:

$$Z = \int_0^1 \frac{(\beta + 1)x}{(1 + \beta x)} dx$$

Integrating the above expression for Z:

$$Z = \beta + 1 \left[\frac{x}{\beta} - \frac{1}{\beta^2} \ln(1 + \beta x) \right]_0^1$$

$$Z = (\beta + 1) \left[\frac{1}{\beta} - \frac{1}{\beta^2} \ln(1 + \beta) \right]_0^1$$

Or, in terms of the separation factor, α :

$$Z = \frac{\alpha}{(\alpha - 1)} - \frac{\alpha}{(\alpha - 1)^2} \ln \alpha$$

Then, solving for R_A in terms of α

$$R_A = \frac{Z}{1 - Z} = \frac{\frac{(\alpha^2 - \alpha - \alpha \ln \alpha)}{(\alpha - 1)^2}}{1 - \frac{(\alpha^2 - \alpha - \alpha \ln \alpha)}{(\alpha - 1)^2}}$$

The above expression can't be solved explicitly for α , so, after R_A is experimentally determined, the best fit α is obtained by trial and error or from a plot of R_A vs α .

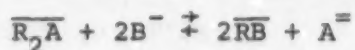
Justification for Use of α_A^B and Not K_A^B

The separation factor α_A^B indicates directly the preference of a given phase, in this case the resin, for the superscript ion in question. It is the ratio of the distribution of ion A to that of ion B.

$$\alpha_B^A = \frac{\text{ratio of fractions of ion A between solid and liquid}}{\text{ratio of fractions of ion B between solid and liquid}}$$

Although the experimentally determined separation factors for divalent/monovalent (SO_4/NO_3) exchange were not constant, the ratio of areas technique has provided a means by which a best fit factor can be determined. This then represents the preference the resin has for one ion over another over the entire range of equivalent fractions at some constant total concentration.

The selectivity coefficient K_A^B at constant total concentration C_0 is the ratio of the squared distribution of the monovalent species to the distribution of the divalent species; as such it is influenced by the units of Q , resin capacity, and C_0 , the total liquid phase concentration. Consider the following example of univalent-divalent exchange:



$$K_A^B = \left[\frac{\overline{\text{B}}}{\text{B}} \right]^2 \left[\frac{\text{A}}{\overline{\text{A}}} \right]$$

$$K_A^B = \frac{C_0}{Q} \left[\frac{y_B}{x_B} \right] \left[\frac{x_A}{y_A} \right]$$

Assuming the resin has no real preference for either ion, then:

$$y_B = x_B$$

$$y_A = x_A$$

$$K_A^B = \frac{C_0}{Q}$$

Typically $Q = 1 \text{ eq/l resin}$ and $C_0 = 0.005 \text{ eq/l solution}$. Then:

$$K_A^B = 0.005$$

If the units of C_0 are given as meq/l then:

$$K_A^B = 5$$

Either of the above choices of units for C_0 yields a selectivity coefficient which infers a large preference by the resin phase, first for ion A then for B neither inference being correct, as the resin has equal affinity for each ion. The separation factor being independent of C_0 and Q correctly infers no preference with $\alpha_A^B = 1.0$.

E4: COLUMN EFFICIENCY

EXAMPLE CALCULATION

Run No: 7, $\alpha_S^N + \alpha_{Cl}^N = 3.54$

Resin: Ionac AFP-100, STY-DVB(I) MR

Resin Volume: .310 l/BV; Flow Rate: 20 BV/hr.

Titration Capacity: meq/ml @ pH 2.3: HCl = 1.07

BV @ 0.48 meq/l NO_3^- -Breakthrough = 295

$$\frac{\text{meq}}{\text{in}^2} = 1500 \frac{\text{meq} \cdot \text{BV}}{1} \times \frac{.310}{\text{BV}} \times \frac{1}{29.98 \text{ in}^2} = \underline{15.51}$$

HCO_3^- Influent Conc: 1.0 meq/l

HCO_3^- Influent Area: 5.906 in² * 15.51 meq/in² = 91.594 meq

HCO_3^- Effluent Area: 5.74 in² * 15.51 meq/in² = 89.027 meq

H_2CO_3 on Resin = 2.57 meq

Cl^- Influent Conc: 1.5 meq/l $Q_{Cl} V = \underline{+331.70}$

Cl^- Influent Area: 8.858 in² * 15.51 meq/in² = 137.39 meq

Cl^- Effluent Area: 27.34 in² * 15.51 meq/in² = 424.04 meq

HCl on Resin = 45.05 meq

NO_3^- Influent Conc: 1.5 meq/l

NO_3^- Influent Area: 8.858 in² * 15.51 meq/in² = 137.39 meq

NO_3^- Effluent Area: .21 in² * 15.51 meq/in² = 3.26 meq

HNO_3 on Resin = 134.13 meq

SO_4^{2-} Influent Conc: 1.5 meq/l

SO_4^{2-} Influent Area: 8.858 in² * 15.51 meq/in² = 137.39 meq

H_2SO_4 on Resin = 137.39 meq

i	Anion	meq on Resin	Eff. Y_i	meq/l in Solution	x_i	Relative Eff. Y_i/x_i
1	HCO_3^-	2.57	.01	1.0	.181	.055
2	Cl^-	45.05	.14	1.5	.273	.513
3	NO_3^-	134.13	.42	1.5	.273	1.54
4	SO_4^{2-}	137.39	.43	1.5	.273	1.58
	Total	319.14	1.0	5.5	1.0	

E5: COLUMN EFFICIENCY

EXAMPLE CALCULATION

Run No: 11, $\alpha_S^N + \alpha_{Cl}^N = 3.97$

Resin: Amberlite IR-45, STY-DVB, Polyamine, Microporous Resin

Resin Volume: .310 l/BV; Flow Rate: 20 BV/hr.

Titration Capacity: meq/l @ pH 2.3: HCl - 1.70, HNO₃ = 1.70,
H₂SO₄ = 2.13

BV @ 0.48 meq/l NO₃-Breakthrough = 480

$$1500 \frac{\text{meq}}{1} \text{BV} * \frac{.310}{\text{BV}} * \frac{1}{29.77 \text{in}^2} = \underline{15.619 \frac{\text{meq}}{\text{in}^2}}$$

HCO₃⁻ Influent Conc: 1.0 meq/l

HCO₃⁻ Influent Area: 9.543 in² * 15.619 meq/in² = 149.057 meq

HCO₃⁻ Effluent Area: 8.69 in² * 15.619 meq/in² = 135.729 meq

H₂CO₃ on Resin = 13.33 meq

Cl⁻ Influent Conc: 1.5 meq/l

Cl⁻ Influent Area: 14.315 in² * 15.619 meq/in² = 223.585 meq

Cl⁻ Effluent Area: 11.62 in² * 15.619 meq/in² = 181.493 meq

HCl on Resin = 42.09 meq

NO₃⁻ Influent Conc: 1.5 meq/l

NO₃⁻ Influent Area: 14.315 in² * 15.619 meq/in² = 223.585 meq

NO₃⁻ Effluent Area: .20 in² * 15.619 meq/in² = 3.124 meq

HNO₃ on Resin = 220.46 meq

SO₄⁼ Influent Conc: 1.5 meq/l

SO₄⁼ Influent Area: 14.315 in² * 15.619 meq/in² = 223.585 meq

H₂SO₄ on Resin = 223.59 meq

i	Anion	meq on Resin	y _i	meq/l in Solution	x _i	Relative Eff. y _i /x _i
1	HCO ₃ ⁻	13.33	.03	1.0	.181	.166
2	Cl ⁻	42.09	.08	1.5	.273	.293
3	NO ₃ ⁻	220.46	.44	1.5	.273	1.612
4	SO ₄ ⁼	223.59	.45	1.5	.273	1.648
	Total	499.47	1.0	5.5	1.0	

E6: EXAMPLE CALCULATION OF PREDICTED $\bar{y}_N$

Objective: To predict $\bar{y}_N = \frac{\text{Meq NO}_3}{\text{meq total on resin at nitrate breakthrough}}$

Assumptions:

- $\sum_i x_i = 1.0, \sum_i y_i = 1.0$
- Constant separation factors, α_j^i 's.
- Three plateau zones
- Two abrupt transition zones
- Instantaneous equilibrium
- $Q \gg C_0$: $Q = 1.0 \text{ meq/ml}, C_0 = .005 \text{ meq/ml}$
- Bicarbonate separation factor $\ll 1.0$: $\alpha_B^N \ll 1.0$

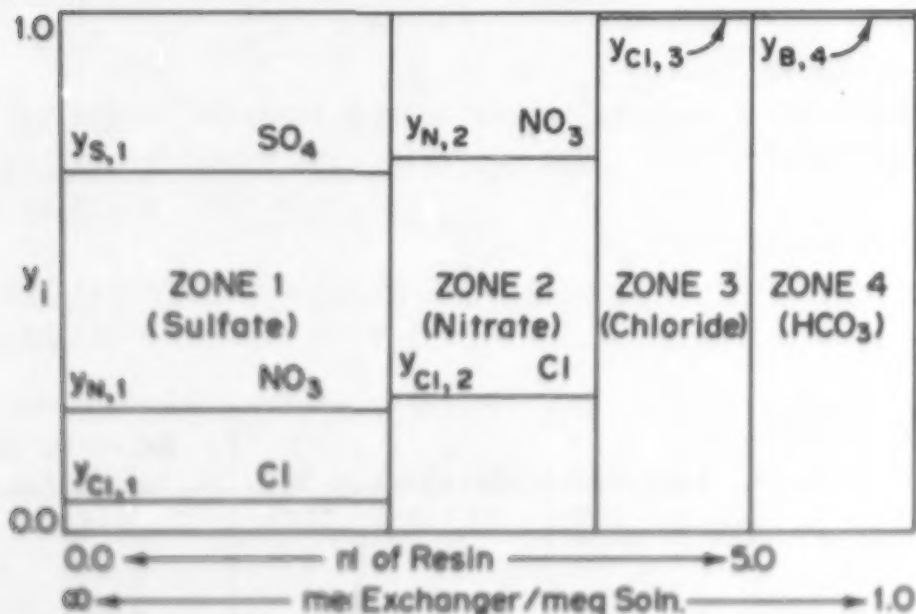


FIGURE E2
RESIN PHASE CONCENTRATION PROFILE

Relevant Equations:

$$(a) \quad \alpha_j^i = \frac{x_i y_j}{y_i x_j}$$

$$(b) \quad y_j = \frac{x_j}{\sum_i \alpha_j^i x_i}$$

$$(c) \quad L_{S,n} + L_{N,n} + L_{Cl,n} = \text{meq entering zone } n \\ = 5 \text{ meq for zone } 1$$

$$(d) \quad S_{S,n} + S_{N,n} + S_{Cl,n} = \text{meq on resin in zone } n$$

Initial Conditions:

$x_{N,1} = .25$	These conditions are equivalent to those existing during Run 1 with the assumption that HCO_3^- is a non-component, an assumption justified on the basis that at equilibrium there is insignificant HCO_3^- (or H_2CO_3) in any zone of interest.
$x_{Cl,1} = .375$	
$x_{S,1} = .375$	
$\alpha_N^N = 1.0$	
$\alpha_N^{Cl} = .26$	
$\alpha_N^S = 2.83$	

Resin capacity = 1 meq/ml.

Calculations:

- (a) Find the equivalent fractions of NO_3 , SO_4 and Cl on the resin in zone 1.

$$y_{N,1} = \frac{x_N}{\alpha_N^S x_S + \alpha_N^N x_N + \alpha_N^{Cl} x_{Cl}}$$

$$y_{N,1} = \frac{.25}{(2.83) (.375) + (1) (.25) + (.26) (.375)}$$

$$y_{N,1} = .18$$

Given $y_{N,1} = .18$ and assuming constant separation

factors, find $y_{S,1}$ and $y_{Cl,1}$.

$$\alpha_N^S = \frac{y_S x_N}{x_S y_N} \quad \text{thus} \quad y_S = \alpha_N^S \frac{x_S y_N}{x_N}$$

$$y_{S,1} = \frac{(2.83) (.375) (.18)}{(.25)}$$

$$y_{S,1} = .75$$

$$\alpha_N^{Cl} = \frac{y_{Cl} x_N}{x_{Cl} y_N} \quad \text{thus} \quad y_{Cl} = \alpha_N^{Cl} \frac{x_{Cl} y_N}{x_N}$$

$$y_{Cl,1} = \frac{(.26) (.375) (.18)}{(.25)}$$

$$y_{Cl,1} = .07$$

(b) Given 5 meq total in liquid entering zone 1 and equivalent fractions in liquid in zone 1, find meq of each component in the liquid.

$$L_{Cl,1} = x_{Cl,1} (5\text{meq}) = 1.875 \text{ meq}$$

$$L_{H,1} = x_{H,1} (5\text{meq}) = 1.25 \text{ meq}$$

$$L_{S,1} = x_{S,1} (5\text{meq}) = 1.875 \text{ meq}$$

- (c) Assuming all SO_4 removed in zone 1, find ml resin in zone 1.

$$(L_{S,1}) \frac{1}{y_{S,1}} (\text{resin capacity}) = \text{ml resin zone 1}$$

$$(1.875 \text{ meq } \text{SO}_4) \frac{1.0 \text{ meq total}}{.64 \text{ meq } \text{SO}_4} \frac{1 \text{ ml resin}}{1 \text{ meq total}} = 2.5 \text{ ml resin}$$

The meq of NO_3 and Cl removed in zone 1 can be found:

$$S_{\text{Cl},1} = Y_{\text{Cl},1} (2.5 \text{ meq}) = (.07) (2.5 \text{ meq}) = .175 \text{ meq Cl}$$

$$S_{\text{N},1} = Y_{\text{N},1} (2.5 \text{ meq}) = (.18) (2.5 \text{ meq}) = .45 \text{ meq } \text{NO}_3$$

- (d) From above, find the meq of NO_3 and Cl remaining in the liquid and hence entering zone 2.

$$L_{\text{Cl},2} = L_{\text{Cl},1} - S_{\text{Cl},1} = 1.875 - .175 = 1.7 \text{ meq Cl}$$

$$L_{\text{N},2} = L_{\text{N},1} - S_{\text{N},1} = 1.25 - .45 = .8 \text{ meq } \text{NO}_3$$

The equivalent fractions of Cl and NO_3 in the liquid entering zone 2 are:

$$E_{\text{Cl},2} = \frac{L_{\text{Cl},2}}{L_{\text{N},2} + L_{\text{Cl},2}}$$

$$E_{\text{Cl},2} = \frac{1.7}{.8 + 1.7}$$

$$E_{\text{Cl},2} = .68$$

$$x_{N,2} = \frac{L_{N,2}}{L_{N,2} + L_{Cl,2}}$$

$$x_{N,2} = \frac{.8}{.8 + 1.7}$$

$$x_{N,2} = .32$$

- (e) Using constant separation factors and the equivalent fractions in the liquid entering zone 2, find the equivalent fractions on the resin in zone 2.

$$y_N = \frac{x_N}{\alpha_N^N x_N + \alpha_N^{Cl} x_{Cl}}$$

$$y_{N,2} = \frac{.32}{(1) (.32) + (.26) (.68)}$$

$$y_{N,2} = .64$$

From constant separation factor $y_{Cl,2}$ is calculated.

$$\alpha_N^{Cl} = \frac{y_{Cl} x_N}{x_{Cl} y_N} \quad \text{thus } y_{Cl} = \alpha_N^{Cl} \frac{x_{Cl} y_N}{x_N}$$

$$y_{Cl,2} = \frac{(.26) (.68) (.64)}{(.32)}$$

$$y_{Cl,2} = .36$$

- (f) Assuming all remaining NO_3 is removed in zone 2, find ml resin in zone 2.

$$(L_{N,2}) \frac{1}{Y_{N,2}} (\text{resin capacity}) = \text{ml resin zone 2}$$

$$(.8 \text{ meq NO}_3) \frac{1 \text{ meq total}}{.64 \text{ meq NO}_3} \frac{1 \text{ ml resin}}{1 \text{ meq total}} = 1.25 \text{ ml resin}$$

1.25 ml resin is equivalent to the removal of 1.25 meq total.

The meq of Cl removed in zone 2 can now be found.

$$S_{Cl,2} = Y_{Cl,2} (1.25 \text{ meq}) = (.36) (1.25) = .45 \text{ meq}$$

- (g) The liquid entering zone 3 contains the following meq of Cl.

$$L_{Cl,3} = L_{Cl,2} - S_{Cl,2} = 1.7 - .45 = 1.25 \text{ meq}$$

Since all the chloride is removed in zone 3 and the resin capacity is 1 meq/ml resin, zone 3 must contain 1.25 ml of resin.

- (h) Find $\bar{Y}_N$ which represents the average of the equivalent fractions of NO_3 on the resin in zones 1 and 2. This is found by weighting the value of Y_N with respect to the amount of resin in the zone in which it occurs.

$$\bar{Y}_N = \frac{(Y_{N,1}) (\text{ml resin zone 1}) + (Y_{N,2}) (\text{ml resin zone 2})}{\text{ml resin zone 1} + \text{ml resin zone 2}}$$

$$\bar{Y}_N = \frac{(.18) (2.5) + (.64) (1.25)}{2.5 + 1.25}$$

$$\bar{Y}_N = .333 \text{ Predicted}$$

$$\bar{Y}_N = .340 \text{ Experimentally Observed (Run 1)}$$

APPENDIX F
STATISTICAL RESULTS

TABLE F1 DATASET FOR STATISTICAL ANALYSIS														
RESIN NUMBER	$\ln^a N_s$ (V1)	$^3N_{Cl}$ (V2)	CAPACITY (V3)	pKa (V4)	FUNCTIONALITY (V5)	MATRIX (V6)	POROSITY (V7)	NITROGEN IN OR OUT (V8)	$\ln^a N_s$ (V9)	$\ln^a N_{Cl}$ (V10)	"R" GROUP SIZE (V11)	NITROGEN POSITION (V12)	TYPE 1 OR 2 (V13)	RELATIVE DEGREE XLINKING (V14)
1	3.75	4.86	.98	7.70	3.00	1.00	2.00	2.00	1.32	1.58	2.19	0.	0.	2.00
2	23.40	1.89	1.42	11.10	3.00	2.00	1.00	1.00	3.15	.64	2.19	1.00	0.	1.00
3	12.70	3.89	1.76	7.90	2.00	1.00	1.00	2.00	3.54	1.36	2.00	0.	0.	1.00
4	137.00	1.95	1.53	7.90	2.00	4.00	1.00	1.00	4.92	.69	2.00	1.00	0.	1.00
5	2.67	4.43	1.15	7.60	3.00	1.00	2.00	2.00	.98	1.49	2.19	0.	0.	2.00
6	108.00	3.35	1.67	7.70	2.00	3.00	2.00	1.00	4.68	1.21	2.00	1.00	0.	2.00
7	82.90	1.70	2.54	8.70	2.00	4.00	1.00	1.00	4.42	.53	2.00	1.00	0.	1.00
8	2.83	3.87	1.43	7.80	3.00	1.00	2.00	2.00	1.04	1.35	2.19	0.	0.	2.00
9	109.00	2.65	1.22	6.80	2.00	3.00	2.00	1.00	4.69	.97	2.00	1.00	0.	2.00
10	94.00	3.85	2.59	9.90	2.00	2.00	2.00	1.00	4.54	1.35	2.00	1.00	0.	2.00
11	54.00	2.25	1.81	10.60	2.00	5.00	1.00	1.00	3.99	.81	2.00	1.00	0.	1.00
12	3.07	4.14	1.24	8.50	3.00	1.00	2.00	2.00	1.12	1.42	2.19	0.	0.	2.00
13	108.00	0.	1.51	9.00	2.00	4.00	1.00	1.00	4.68	0.	2.00	1.00	0.	1.00
14	3.26	2.85	1.31	13.00	4.00	1.00	2.00	2.00	1.18	1.05	2.36	0.	2.00	2.00
15	1.89	0.	1.53	13.00	4.00	1.00	1.00	2.00	.64	0.	2.36	0.	1.00	1.00
16	3.09	3.11	1.16	13.00	4.00	1.00	3.00	2.00	1.13	1.13	2.36	0.	1.00	.50
17	1.71	3.41	1.10	13.00	4.00	1.00	2.00	2.00	.54	1.23	2.36	0.	1.00	2.00
18	2.40	0.	1.35	13.00	4.00	1.00	1.00	2.00	.88	0.	2.36	0.	2.00	1.00
19	2.96	0.	1.02	13.00	4.00	1.00	3.00	2.00	1.09	0.	2.36	0.	1.00	.50
20	3.04	0.	1.50	13.00	4.00	1.00	1.00	2.00	1.11	0.	2.36	0.	2.00	1.00
21	1.89	2.90	1.66	13.00	4.00	1.00	1.00	2.00	.64	1.06	2.36	0.	1.00	1.00
22	3.37	0.	1.17	13.00	4.00	1.00	3.00	2.00	1.21	0.	2.36	0.	1.00	.50
23	3.26	0.	1.48	13.00	4.00	1.00	1.00	2.00	1.18	0.	2.36	0.	2.00	1.00
24	2.59	0.	1.32	13.00	4.00	1.00	3.00	2.00	.95	0.	2.36	0.	1.00	.50
25	0.	0.	0.	13.00	4.00	1.00	0.	0.	0.	0.	2.36	0.	0.	0.
26	0.	0.	0.	13.00	4.00	1.00	0.	0.	0.	0.	2.36	0.	0.	0.
27	1.87	0.	1.39	13.00	4.00	1.00	1.00	2.00	.63	0.	2.36	0.	1.00	1.00
28	3.33	3.33	1.21	13.00	4.00	1.00	3.00	2.00	1.20	1.20	2.36	0.	1.00	.50
29	3.04	3.64	1.13	13.00	4.00	1.00	1.00	2.00	1.11	1.29	2.36	0.	2.00	1.00
30	2.59	0.	1.13	13.00	4.00	1.00	3.00	2.00	.95	0.	2.36	0.	1.00	.50
31	0.	0.	0.	13.00	4.00	1.00	0.	0.	0.	0.	2.36	0.	0.	0.
32	1.76	2.77	1.07	13.00	4.00	1.00	2.00	2.00	.57	1.00	2.36	0.	1.00	2.00

TABLE F2
CORRELATION MATRIX FOR WEAK-BASE RESINS

CORRELATION COEFFICIENTS CASES=CASE#:1-13

N= 12 DF= 10 R₀ .0500= .5760 R₀ .0100= .7079

VARIABLE							
3. CAPACITY	1.0000						
4. PKA	.4175	1.0000					
9. LOG _e S/N	.5774	.1824	1.0000				
10. LOG _e N/CL	-.3728	-.4231	-.6725	1.0000			
11. RSIZE	-.6336	.0155	-.8651	.4296	1.0000		
12. N2POSITN	.5157	.4104	.9315	.7754	.6571	1.0000	
14. XLINKING	-.3446	.4813	-.3732	.7466	.3714	.3714	1.0000
3. CAPACITY	4. PKA	9. LOG _e S/N	10. LOG _e N/CL	11. RSIZE	12. N2POSITN	14. XLINKING	

TABLE F3
CORRELATION MATRIX FOR STRONG-BASE RESINS

CORRELATION COEFFICIENTS CASES=CASE#:14-32

N= 7 DF= 5 R₀ .0500= .7545 R₀ .0100= .8745

VARIABLE				
3. CAPACITY	1.0000			
9. LOG _e S/N	.0191	1.0000		
10. LOG _e N/CL	-.2806	.1677	1.0000	
14. XLINKING	-.2743	-.5367	-.2808	1.0000
3. CAPACITY	9. LOG _e S/N	10. LOG _e N/CL	14. XLINKING	

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TABLE F4
CORRELATION MATRIX FOR ALL ANION RESINS

CORRELATION COEFFICIENTS

N= 19 DF= 17 R₀ .0500= .4555 R₀ .0100= .5751

VARIABLE	1.S04/N03	2.N03/CL	3.CAPACITY	4.PKA	9.LOG _e S/N	10.LOG _e N/CL	11.RSIZE	12.N2POSITN	14.XLINKING
1.S04/N03	1.0000								
2.N03/CL	-.4652	1.0000							
3.CAPACITY	.5311	-.3303	1.0000						
4.PKA	-.5094	-.2051	-.1940	1.0000					
9.LOG _e S/N	.9413	-.5002	.6332	-.5298	1.0000				
10.LOG _e N/CL	-.4813	.9884	-.3596	-.1231	-.5319	1.0000			
11.RSIZE	-.7901	.1952	-.6090	.7973	-.8825	.2540	1.0000		
12.N2POSITN	.8824	-.6202	.5964	-.3876	.9485	-.6522	-.7683	1.0000	
14.XLINKING	.0369	.4576	-.1602	-.3663	-.0689	.4520	-.0973	-.0601	1.0000
1.S04/N03		2.N03/CL	3.CAPACITY	4.PKA	9.LOG _e S/N	10.LOG _e N/CL	11.RSIZE	12.N2POSITN	14.XLINKING

TABLE F5
CORRELATION MATRIX FOR POLYSTYRENE RESINS

CORRELATION COEFFICIENTS STRAT=NITROGEN:2

N= 12 DF= 10 R₀ .0500= .5760 R₀ .0100= .7079

VARIABLE							
3.CAPACITY	1.0000						
4.PKA	-.1058	1.0000					
9.LOG _e S/N	.4927	-.4850	1.0000				
10.LOG _e N/CL	-.1937	-.8643	.3587	1.0000			
11.RSIZE	-.3812	.8991	-.7583	-.7054	1.0000		
12.N2POSITN	-0.	-0.	-0.	-0.	-0.	0.	
14.XLINKING	-.3611	-.4127	-.3008	.3338	-.1915	-0.	1.0000
	3.	4.	9.	10.	11.	12.	14.
	CAPACITY	PKA	LOG _e S/N	LOG _e N/CL	RSIZE	N2POSITN	XLINKING

TABLE F6
CORRELATION MATRIX FOR NON-POLYSTYRENE RESINS

CORRELATION COEFFICIENTS STRAT=NITROGEN:1

N= 7 DF= 5 R₀ .0500= .7545 R₀ .0100= .8745

VARIABLE							
3.CAPACITY	1.0000						
4.PKA	.2798	1.0000					
9.LOG _e S/N	.1345	.8190	1.0000				
10.LOG _e N/CL	-.1586	-.1757	.3786	1.0000			
11.RSIZE	.3324	.5861	.8740	-.3595	1.0000		
12.N2POSITN	-0.	-0.	-0.	-0.	-0.	-0.	
14.XLINKING	.0017	-.4780	.4628	.8943	-.3536	0.	1.0000
	3.	4.	9.	10.	11.	12.	14.
	CAPACITY	PKA	LOG _e S/N	LOG _e N/CL	RSIZE	N2POSITN	XLINKING

SELECTION OF REGRESSION CASES=CASE#11-13

LOG OF SULFATE/NITRATE SELECTIVITY RELATED TO ALL THE INDEPENDENT
VARIABLES OF INTEREST FOR WEAK-BASE ANION RESINS--OPTIMIZATION
ANALYSIS AT STEP 1 FOR 9.LOG S N N= 13 OUT OF 13

<u>SOURCE</u>	<u>DF</u>	<u>SUM OF SQRS</u>	<u>MEAN SQUARE</u>	<u>F-STAT</u>	<u>SIGNIF</u>
REGRESSION	1	27.385	27.385	76.282	.0000
ERROR	11	3.9489	.35899		
TOTAL	12	31.334			

MULTIPLE R= .93486 R-SQR= .87397 SE= .59916

<u>VARIABLE</u>	<u>PARTIAL</u>	<u>COEFFICIENT</u>	<u>STD ERROR</u>	<u>T-STAT</u>	<u>SIGNIF</u>
CONSTANT		1.4015	.26795	5.2303	.0003
12.N2POSITN	.93486	2.9833	.34157	8.7340	.0000

<u>REMAINING</u>	<u>PARTIAL</u>	<u>SIGNIF</u>
3.CAPACITY	.25354	.4265
11.RSIZE	-.92235	.0000
14.V14	-.11621	.7191

ANALYSIS AT STEP 2 FOR 9.LOG S N N= 13 OUT OF 13

<u>SOURCE</u>	<u>DF</u>	<u>SUM OF SQRS</u>	<u>MEAN SQUARE</u>	<u>F-STAT</u>	<u>SIGNIF</u>
REGRESSION	2	30.744	15.372	260.80	.0000
ERROR	10	.58943	.58943 -1		
TOTAL	12	31.334			

MULTIPLE R= .99055 R-SQR= .98119 SE= .24278

<u>VARIABLE</u>	<u>PARTIAL</u>	<u>COEFFICIENT</u>	<u>STD ERROR</u>	<u>T-STAT</u>	<u>SIGNIF</u>
CONSTANT		17.442	2.1275	8.1985	.0000
11.RSIZE	-.92235	-7.4538	.98731	-7.5496	.0000
12.N2POSITN	.95976	2.0274	.18759	10.807	.0000

<u>REMAINING</u>	<u>PARTIAL</u>	<u>SIGNIF</u>
3.CAPACITY	-.39349	.2312
14.V14	.18226	.5917

REGRESSION OF 9.LOG S N USING FORWARD SELECTION

<u>STEP</u>	<u>R-SQR</u>	<u>STD ERROR</u>	<u># VAR</u>	<u>VARIABLE</u>	<u>PARTIAL</u>	<u>SIGNIF</u>
1	.87397	.59916	1	12.N2POSITN	IN .93486	.0000
2	.98119	.24278	2	11.RSIZE	IN -.92235	.0000

SELECTION OF REGRESSION CASES=CASE#11-13

LOG OF NITRATE/CHLORIDE SELECTIVITY RELATED TO ALL THE INDEPENDENT
VARIABLES OF INTEREST FOR WEAK-BASE ANION RESINS--OPTIMIZATION
ANALYSIS AT STEP 1 FOR 10.LOG N CL N= 12 OUT OF 13

<u>SOURCE</u>	<u>DF</u>	<u>SUM OF SQRS</u>	<u>MEAN SQUARE</u>	<u>F-STAT</u>	<u>SIGNIF</u>
REGRESSION	1	.89825	.89825	15.078	.0030
ERROR	10	.59573	.59573 -1		
TOTAL	11	1.4940			

MULTIPLE R = .77540 R-SQR = .60124 SE = .24408

<u>VARIABLE</u>	<u>PARTIAL</u>	<u>COEFFICIENT</u>	<u>STD ERROR</u>	<u>T-STAT</u>	<u>SIGNIF</u>
CONSTANT		1.4404	.10915	13.196	.0000
12.N2POSITN	-.77540	-.55495	.14292	-3.8830	.0030

<u>REMAINING</u>	<u>PARTIAL</u>	<u>SIGNIF</u>
3.CAPACITY	.05000	.8839
11.RSIZE	-.16796	.6216
14.V14	.78221	.0044

ANALYSIS AT STEP 2 FOR 10.LOG N CL N= 12 OUT OF 13

<u>SOURCE</u>	<u>DF</u>	<u>SUM OF SQRS</u>	<u>MEAN SQUARE</u>	<u>F-STAT</u>	<u>SIGNIF</u>
REGRESSION	2	1.2627	.63137	24.574	.0002
ERROR	9	.23123	.25692 -1		
TOTAL	11	1.4940			

MULTIPLE R = .91936 R-SQR = .84522 SE = .16029

<u>VARIABLE</u>	<u>PARTIAL</u>	<u>COEFFICIENT</u>	<u>STD ERROR</u>	<u>T-STAT</u>	<u>SIGNIF</u>
CONSTANT		.75501	.19557	3.8606	.0038
12.N2POSITN	-.80640	-.41353	.10109	-4.0908	.0027
14.V14	.78221	.38075	.10109	3.7666	.0044

<u>REMAINING</u>	<u>PARTIAL</u>	<u>SIGNIF</u>
3.CAPACITY	.32791	.3550
11.RSIZE	-.50651	.1352

REGRESSION OF 10.LOG N CL USING FORWARD SELECTION

<u>STEP</u>	<u>R-SQR</u>	<u>STD ERROR</u>	<u># VAR</u>	<u>VARIABLE</u>	<u>PARTIAL</u>	<u>SIGNIF</u>
1	.60124	.24408	1	12.N2POSITN	IN -.77540	.0030
2	.84522	.16029	2	14.V14	IN .78221	.0044

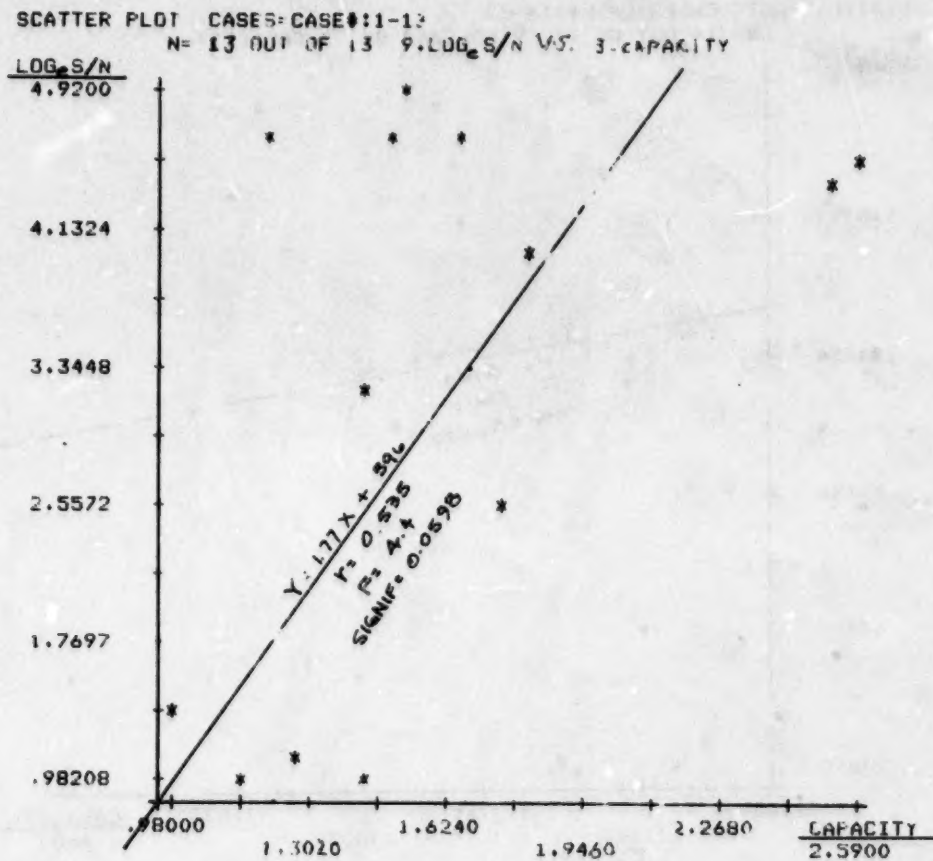


FIGURE F2
SCATTER PLOT WITH LINEAR REGRESSION EQUATION
ln α_N^S vs. MEASURED HCl CAPACITY
FOR
WEAK BASE RESINS ONLY

SCATTER PLOT CASES=CASE#:14-32
 N= 16 OUT OF 19 9.LOG S/N VS. 3.CAPACITY

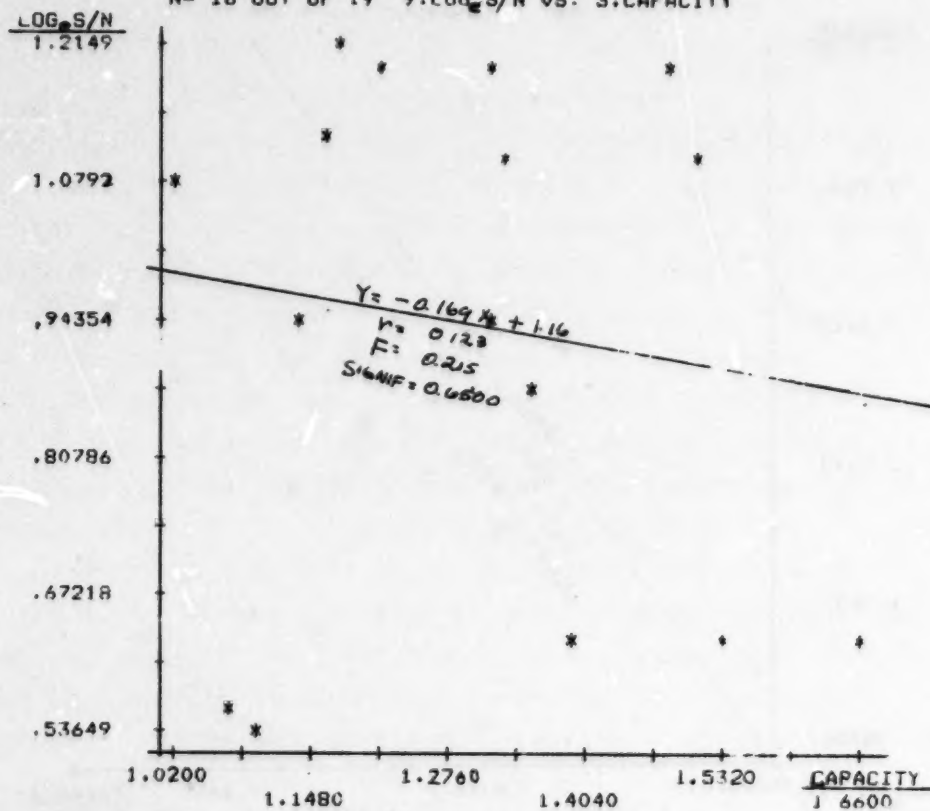


FIGURE F3
 SCATTER PLOT WITH LINEAR REGRESSION EQUATION
 $\ln \alpha_N^S$ vs. MEASURED HCl CAPACITY
 FOR
 STRONG BASE RESINS ONLY

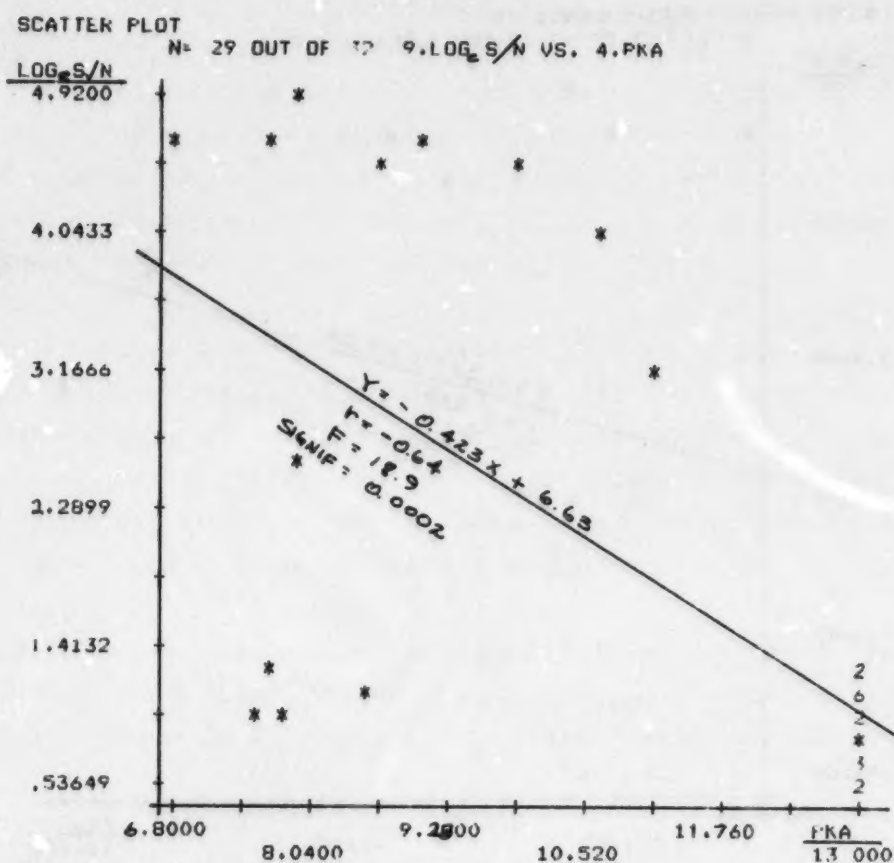


FIGURE F4

SCATTER PLOT WITH LINEAR REGRESSION EQUATION

$\ln \alpha_N^S$ vs. pK_a

FOR

WEAK AND STRONG BASE RESINS

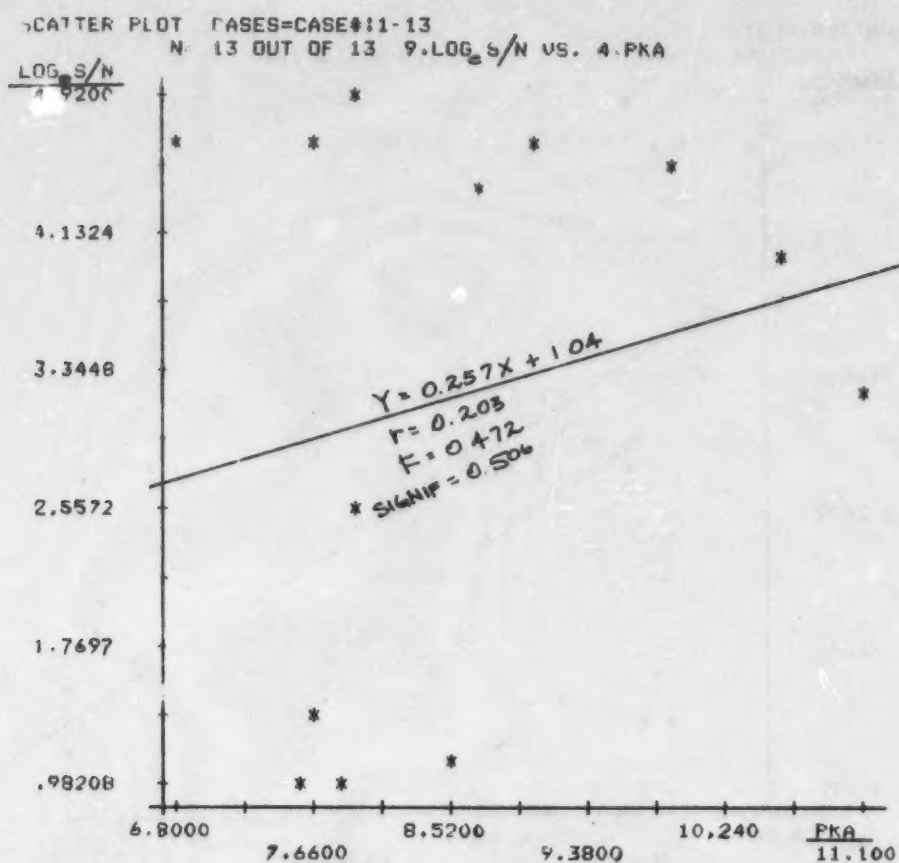


FIGURE F5
SCATTER PLOT WITH LINEAR REGRESSION EQUATION
 $\ln q_N^S$ vs. pK_a
FOR
WEAK BASE RESINS ONLY

SCATTER PLOT STRAT=NITROGEN:
N= 8 OUT OF 8 9. LOG₁₀ S/N VS. PKA

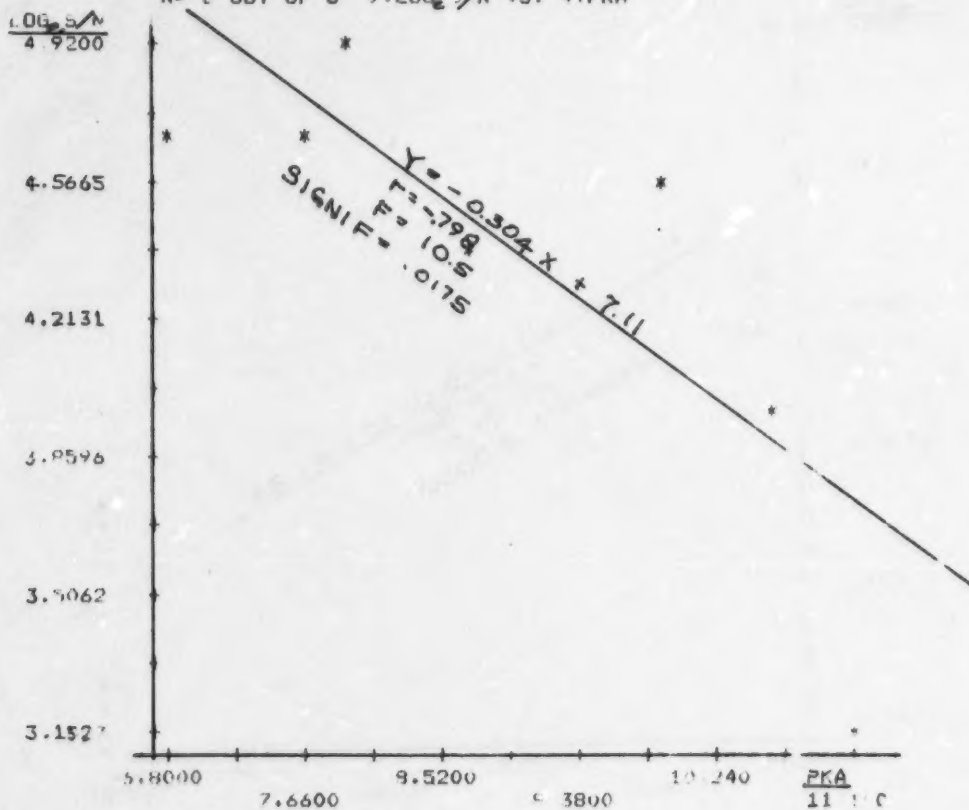


FIGURE F6

SCATTER PLOT WITH LINEAR REGRESSION EQUATION

$\ln \alpha_N^S$ vs. pK_a

FOR

NON-POLYSTYRENE RESINS

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best available copy.



SCATTER PLOT STRAT=MATRIX:1
N= 12 OUT OF 24 10.LOG_e N/CL VS. 4.PKA

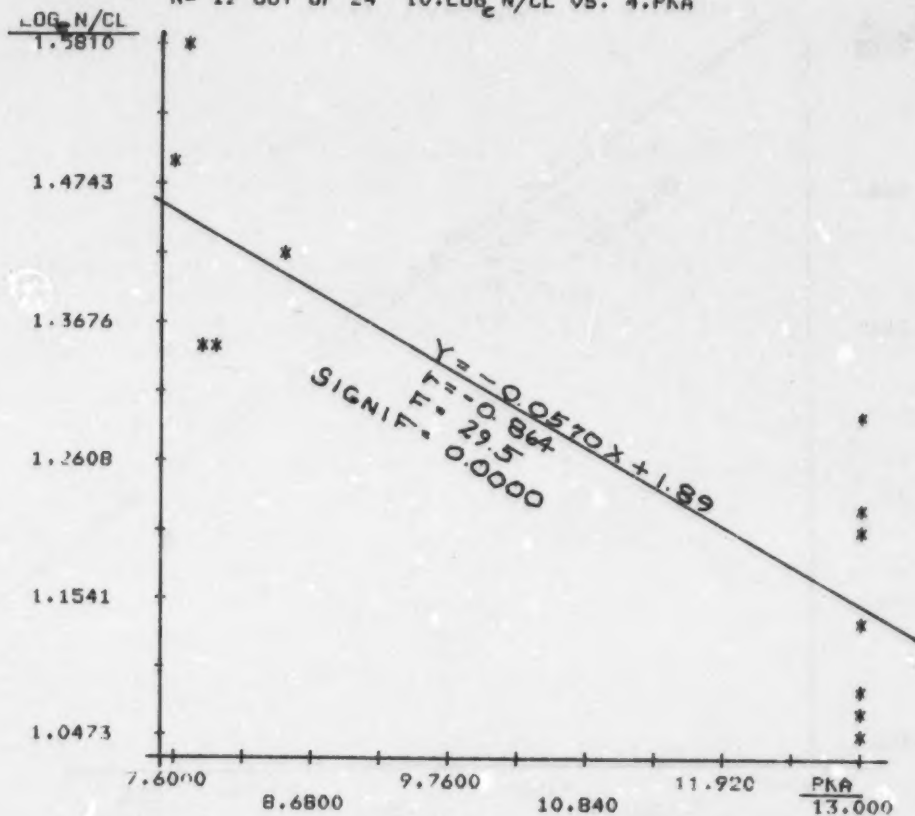


FIGURE F7

SCATTER PLOT WITH LINEAR REGRESSION EQUATION

$\ln \alpha_{Cl}^N$ vs. pK_a

FOR

POLYSTYRENE RESINS

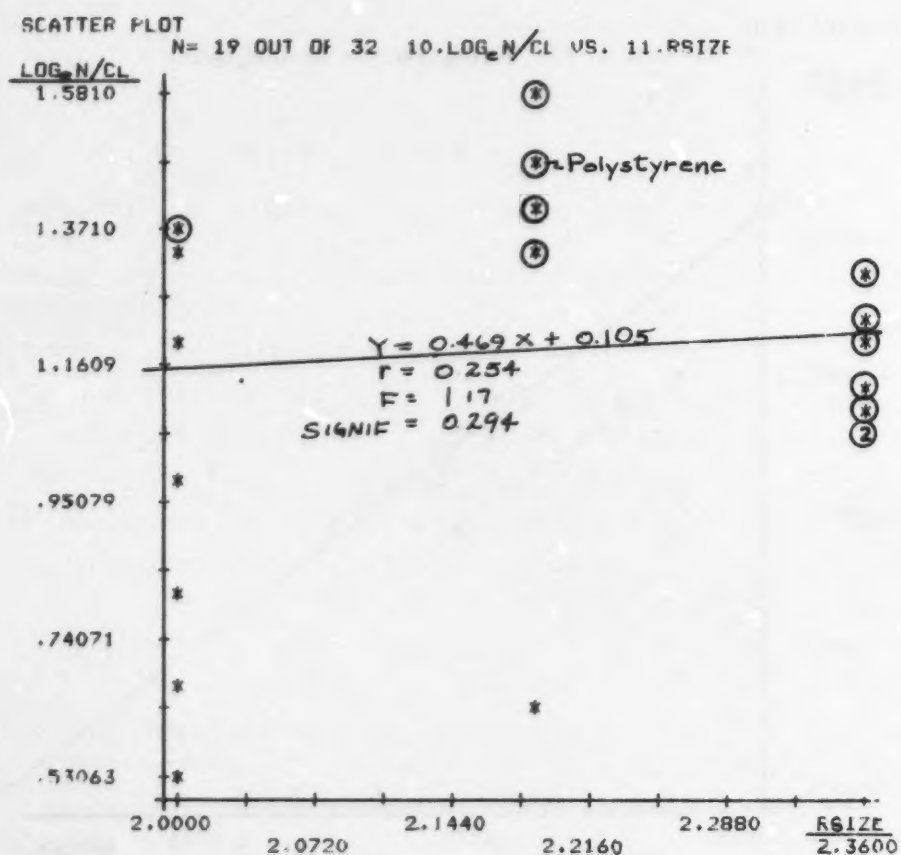


FIGURE F8
SCATTER PLOT WITH LINEAR REGRESSION EQUATION
 $\ln a_{Cl}^N$ vs. FUNCTIONAL GROUP SIZE
FOR
WEAK AND STRONG BASE RESINS

SCATTER PLOT

N: 19 OUT OF 32 9.LOG₁₀ S/N VS. 10.LOG₁₀ N/CL

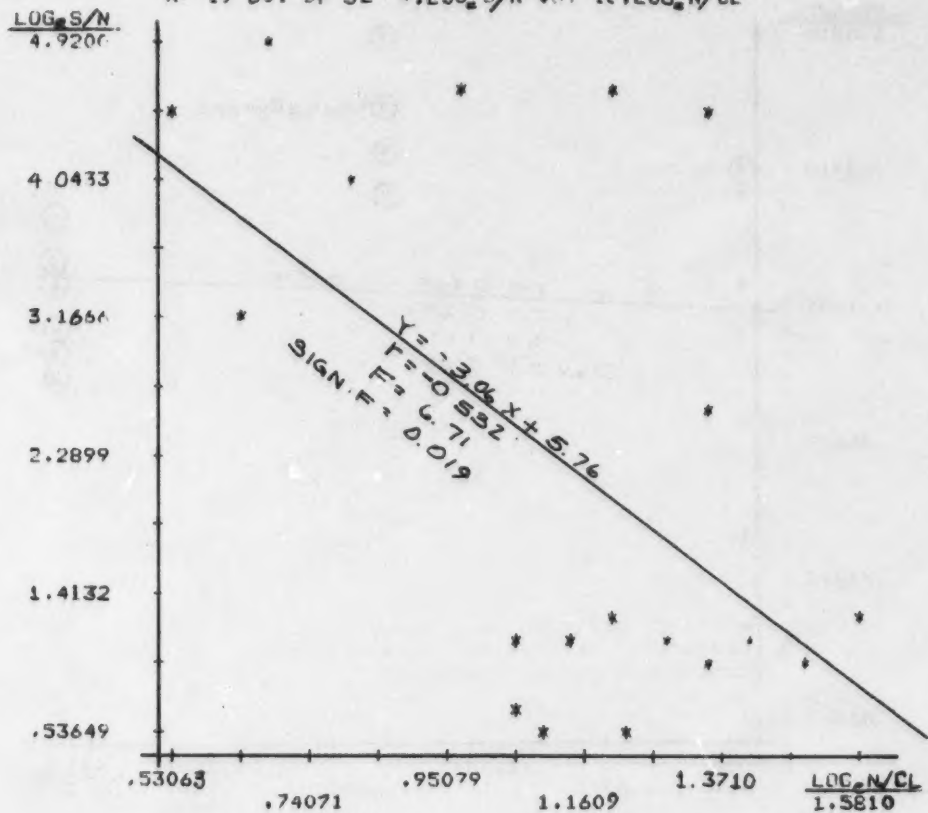


FIGURE F9

SCATTER PLOT WITH LINEAR REGRESSION EQUATION

$\ln a_v^S$ vs. $\ln a_{Cl}^N$

FOR

WEAK AND STRONG BASE PESING

SCATTER PLOT

N= 29 OUT OF 32 11.RSIZE VS. 12.N2POSITN

RSIZE

2.3600

2.2880

2.2160

2.1440

2.0720

2.0000

16

0.

$$Y = -.287 X + 2.31$$

$$R^2 = 0.824$$

$$F = 57.1$$

$$\text{SIGN}(F) = 0.0000$$

Nitrogen position is a dummy variable
presumably related to the distance of
functional group separation

1.00 = Nitrogen in Polymer Backbone

0.00 = Nitrogen Pendant

N2POSITN
1.0000

FIGURE F10

SCATTER PLOT WITH LINEAR REGRESSION EQUATION

FUNCTIONAL GROUP SIZE vs. NITROGEN POSITION

FOR

WEAK AND STRONG BASE RESINS

GLOSSARY

"as CaCO_3 ": Normality (N) can be converted to calcium carbonate equivalents. There are 50 mg of CaCO_3 per milliequivalent. Any 0.005 N solution contains 5 milliequivalents/l or the equivalent of 250 mg/l of CaCO_3 .

bed: The ion-exchange resin contained in a column. Water to be treated by ion-exchange is passed downward through the column.

breakthrough: The appearance of a sharp increase in the concentration of an ion in the effluent from the bed.

capacity: The total number of ion-exchange sites available per unit volume of resin measured in equivalents/l or milliequivalents/ml. Resins were equilibrated with 0.005 N acids (HCl , H_2SO_4 or HNO_3) for the experimental capacity determinations. This was done to simulate the expected capacities in typical groundwater applications.

chromatographic elution: Continued application of the feed water to an exhausted ion-exchange bed so as to "elute" or sequentially drive off those less-preferred feed water anions previously removed during the exhaustion cycle. In this operation, the ions being driven off the resin are separated into zones in which the aqueous concentration of the primary ion in a given zone exceeds the concentration of that ion in the feed water.

downflow regeneration: Cocurrent regeneration, i.e., the regenerant solution is passed down through the bed in the same direction as the feed water was passed through the bed.

effluent profile: A plot of the effluent concentration of an ion or ions vs. the volume of effluent water from the bed.

elution: The displacement of non-preferred ions previously removed from the feed water by continued application of the feed water or an "eluting solution" containing an ion or ions more preferred by the ion exchanger.

equivalent: One gm equivalent (6.023×10^{23}) of ionic charges in the aqueous phase or that number of fixed charges in the resin phase.

equivalent fraction: That fraction of the total negative or positive charges present which is due to a given ion. If $x_s = 0.27$, then 27% of the negative ionic charges in a given volume of water are due to sulfate ions.

exhaustion: The step in an ion-exchange cycle in which the undesirable ions are removed from the water being treated. The resin bed is said to be "exhausted" when the ions originally on the resin have been essentially completely exchanged for feed water ions.

functionality: A description of the nature of the amine groups attached to the resin matrix which give an anion resin its ion exchange properties, e.g., quaternary amine functionality.

ion-exchange: A physicochemical process in which ions in the water being treated replace and are exchanged for ions in a solid phase (the resin). In the single-bed process, nitrate, the pollutant ion, is placed on the resin phase in exchange for an innocuous ion such as chloride.

isoporous resins: Resins having slightly greater uniform porosity than typical microporous resins.

isotherm: A constant temperature plot of resin phase concentration of an ion vs. the water phase concentration of that ion. In a binary isotherm, e.g., sulfate/nitrate, the resin phase exchange sites not occupied by sulfate are occupied by nitrate. Similarly, the significant anions in the water which are not sulfate are nitrate.

macroporous resins (also referred to as macroreticular resins): Very porous resins whose beads comprise aggregates of gel resins with large internal voids having diameters up to several hundred angstroms (A). This porosity is non-uniform with areas of very high crosslinking. Macroporous resin beads are opaque.

matrix: The polymer backbone of a synthetic organic ion-exchange resin.

microporous resins (also referred to as gel resins): resins with porosity of atomic dimensions, i.e., having "pores" which are 10-20 A in diameter. Gel resins are relatively uniform in porosity and the beads are transparent.

milliequivalent: (Abbreviated meq.) 1/1000 of an equivalent.
An 0.005 N solution contains 0.005 equivalents/l or 5 meq/l.

porosity: A measure of the degree of openness of the polymer matrix which is related to the nature and degree of crosslinking.

regeneration: The displacement from the exhausted ion-exchange resin of the undesirable ions removed from the water during the exhaustion cycle. Performed by passing through the bed, a relatively concentrated (1 N) solution of the ion desired on the resin.

regeneration level: A measure of the inefficiency of regeneration expressed here in %. The level indicates the amount of regenerant which must actually be applied compared to the amount theoretically required. For downflow regeneration a level of 300% is typically required; that means a 200% excess of regenerant must be applied.

selectivity: A measure of the relative affinity for one ion over another exhibited by the resin. In this report selectivity (relative affinity) is measured by the separation factor, α . This α should not be confused with the selectivity coefficient, K.

selectivity sequence: A listing of ions as preferred by the ion exchanger ordered from most preferred to least preferred.

separation factor (binary): The ratio of the distribution of ions between the water phase and the resin phase. $\alpha_{S,N}$ is the ratio of the distribution of sulfate ions between phases to the distribution of nitrate ions between phases. If $\alpha_{S,N} \geq 1$, the resin prefers sulfate over nitrate.

service flow rate: The rate of application of feedwater to the resin bed. Because the exchanger capacity is related to the volume of resin, the rate is usually specified as gal/min ft³ or volume of feed water per volume of resin per unit time. With proper units this is reciprocal superficial detention time. Recommended exhaustion rates are 1-5 gal/min ft³ corresponding to detention times of from 7.48 to 1.50 minutes.

softening: In ion exchange, a process by which polyvalent cations, e.g., calcium, magnesium, and iron are exchanged for a monovalent cation such as hydrogen or sodium.

spent regenerant: A wastewater containing the excess regenerant ions and the undesirable ions removed from the exhausted resin. Its volume will be determined by the volume of rinses included as "spent regenerants."

strong-base resin: An anion exchange resin containing fixed positively charged quaternary amine functional groups which prefer all common anions over hydroxide ions. Simply, a resin which tends to readily give up hydroxide ions in exchange for nearly any other anion. The capacity of strong-base resins to exchange ions does not depend on the presence of excess hydrogen ions (acidity) to form the positively charged exchange sites as is the case with weak-base resins. Thus, they may be used as ion exchangers in acid, neutral, and basic solutions.

superficial detention time (τ): The time a particle of feed water spends in the empty resin bed assuming plug flow. It is calculated as the empty bed volume divided by the feed flow rate.

upflow regeneration: Countercurrent regeneration, i.e., the regenerant solution is passed up through the bed in a direction opposite to that taken by the feedwater. Countercurrent regeneration is reportedly more efficient than cocurrent regeneration because the most preferred ions are not driven through the entire bed.

weak-base resin: An ion-exchange resin comprising primary, secondary, or tertiary amine functional groups or a mixture of those groups which acquire positive charges when excess hydrogen ions (acidity) are present. These charged sites can exchange anions if the feed solution remains acidic. Thus, these resins are said to "adsorb" acids. In neutral to basic solutions they have no charged sites and consequently no significant anion exchange capacity. They are readily regenerated with weak bases or even neutral water solutions.